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MCL-659/V

TRANSLATION

FUNDAMENTALS OF STEEL ALLOYING (Selected Parts)

By V. S. MES'KIN

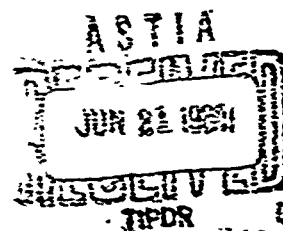
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C. EFFECT OF ALLOYING ON WELDABILITY

Fusion welding of steel, which is the most widespread method at the present time, embodies so many complex processes which depend both on the steel itself and the characteristics of the welded structure, and on the welding conditions, among other things, that thus far there is not even a unified definition of weldability [for example, 650]. Welded structures of low-alloy structural steels must, in the vast majority of cases, not be subjected to subsequent heat treatment for technical or economic reasons. In this case weldability should be understood to mean the possibility of obtaining a welded joint which is not inferior, or only slightly inferior, in strength to the base metal, minimum change in the properties of the base metal in the seam zone, i. e., the zone of thermal action of the weld, and absence of cracks in the seam and seam zone.

For evaluation of the weldability of steel, methods have now been developed for all-round testing of the weld joint, including determination of its tendency toward brittle failure, which is now considered compulsory both at home and abroad [651, 664]. Methods of high-speed testing (including testing with an explosive wave in contact explosion) have been widely developed of late as an additional characteristic of the strength of a welded joint, particularly for steel employed in shipbuilding. For evaluation of the tendency of weld metal to the formation of hot cracks, methods have also been developed which consist in static or dynamic mechanical action on a specimen while it is being welded [652].

Of the criteria referred to above of good weldability of steel, obtaining a welded joint which is not inferior, or very slightly inferior, in strength to the base metal, is achieved at the present time chiefly by "welding" methods: selection of the electrodes, welding conditions, and the like. Thus, the most important criteria of weldability, which are greatly affected by the

composition, and to a certain extent by the initial structure of the steel, include change in the properties of the base metal in the weld zone and the probability of occurrence of weld cracks.

Deterioration of the properties in the weld zone is related to two circumstances: (1) to the possibility of obtaining metastable structures in the process of cooling after welding, and consequently, the hardenability of the steel in terms of depth and distribution of hardness induced by quenching; (2) to coarsening of the grain in the weld zone in weld heating. In welded joints of considerable thickness, the cooling rate in the weld zone or individual points in it may exceed the critical cooling rate of the steel in question, as a result of which martensitic regions may occur in the weld zone, particularly in the case of a single-layer seam. This has in fact been noted by a number of investigators. Brittle failure may be observed in steels in which more martensite forms or in which the latter possesses a higher hardness, when the welded joint is subjected to bend testing.

The danger of occurrence of cold cracks or residual stresses in the welded joint in the same steel also depends on the "welding" factors and may be prevented to a large extent by regulating them [for example, 395]. However, a prominent part in the occurrence of cold cracks and residual stresses is played by the structural transformations in the steel in the process of cooling after welding and by the temperature ranges in which these transformations take place, and this in turn is also related to a great extent to the hardenability of the steel. In particular, obtaining martensitic regions in the welded joint will also reinforce the residual stresses and the danger of occurrence of cracks. Coarsening of the grain in weld heating will have an effect in the same direction, both directly and indirectly, due to increase in the hardenability of the steel. Thus, although deterioration of the properties of the weld zone and the formation of cold cracks are, generally speaking, determined by different factors, these two effects most often accompany each other, under the

influence of alloying as well.

The principle which should govern the effect of the elements on the weldability of steel follows from the foregoing. Indeed, since we must concern ourselves with the change in hardness and other mechanical properties, and since this change is related to the possibility of obtaining martensite in the zone subjected to heating to a high temperature and subsequent rapid cooling, the part played by the alloying elements and carbon contained in the steel in the weldability must be the same as in the case of quenching of the steel.

In the event of full solution of all the phases and the formation of homogeneous austenite, which occurs in welding due to the very high heating temperature, the maximum hardness obtained after quenching, or properly speaking the hardenability, must depend chiefly only on the carbon content of the steel, while the presence of alloying elements in it merely facilitates achievement of maximum hardness. The results obtained in a number of studies confirm the fact that in the case of welding the maximum hardness of the steel is also determined only by its carbon content. The carbon also favors increase in the amount of martensite, by lowering the critical cooling rate in quenching.

It follows that from the standpoint of weldability carbon is one of the most harmful elements in steel. This is the third circumstance in number, but the first in degree of importance, which limits the possibility of using carbon as a strengthening element in low-alloy steels not subjected to refining. In these steels, so as to retain the good weldability, the carbon content is usually 0.001--0.12--0.15% and must not exceed 0.20% if it is impossible prior to welding to preheat the welded elements and after welding to relieve the stresses and improve the plastic properties by heat treatment.

The alloying elements, by lowering the critical cooling rate, contribute to the occurrence of martensite in the welding of relatively thin-walled

structures in which the cooling rate is lower. Thus, at the maximum thickness of welded elements of low-alloy steels of increased strength encountered under practical conditions, the cooling rate of the seam zone is 30 to 50 degrees per second, i. e., much lower than the critical cooling rate for carbon steel, even that with a high carbon content. On the other hand, if alloying elements are present in the steel, a cooling rate of 30 to 50 degrees per second may prove to be near, equal to, or even greater than the critical rate.

Hence, the effect of a given alloying element on the weldability of steel, other conditions being equal, must be the greater, the more greatly does this element increase the hardenability of the steel [see also 308]. In accordance with the values of the conversion factors for hardenability given on Text page 161, the least deterioration of the weldability of steel should be caused by nickel, copper, silicon, while manganese, chromium, and molybdenum should have the greatest effect in this direction (each element being present in the steel separately); this is confirmed in the main by experiments.

Similar factors may be found experimentally to determine the quantitative effect of alloying elements on the weldability of steel. For this purpose, use may be made in the first approximation of the Jominy method, which permits finding the interrelation between hardness and cooling rate over a wide range, if the weldability is to be evaluated only on the basis of increase in hardness and not on the basis of change in the mechanical properties. Thus, for example, in our studies¹ the end quench method² was used for studying the effect of silicon, manganese, and chromium on the weldability of steel with two carbon content levels: 0.15-0.17% and 0.21-0.23%. A parallel study was also made of the increase in hardness immediately in the seam zone and

¹In collaboration with K. V. Petran' and L. P. Kopp.

²A grooved specimen (an L specimen; see page 152) suitable for study of the hardenability of shallow hardening steels was used.

the ability of the steels to regain their plastic properties in the seam zone. The effect of the elements referred to, as well as of carbon, on increase in the hardness in the seam zone is illustrated by Figure 240, from which it is to be seen that the maximum hardness is obtained in the steel alloyed with chromium and the minimum hardness in the steel alloyed with silicon. This was also confirmed with end quench specimens, i. e., at various cooling rates, thus attesting to the adequate reliability of this method.

For a relative characteristic of the weldability of steels alloyed simultaneously with several elements and containing varying amounts of carbon, use may also be made of the value of the ideal critical diameter, which characterizes hardenability. The greater the ideal critical diameter, the worse will be the weldability of a given steel, all other conditions being equal. The ideal critical diameter also makes allowance for the effect of such an important factor as grain size, the effect being the greater, the greater is the grain size, all other conditions being equal.

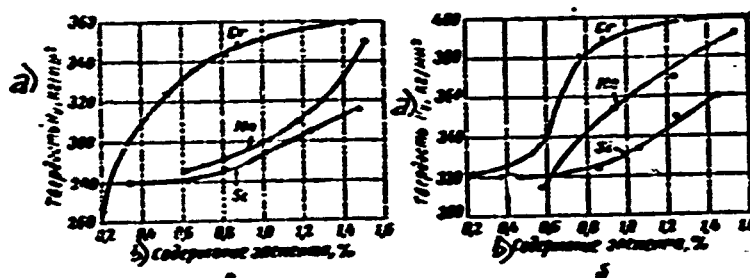


Figure 240. Effect of silicon, manganese, and chromium on increase in hardness of seam zone in steel with 0.15% C (a) and 0.22% C (b). (a) Hardness H_v , kg/mm²; (b) content of element, %.

It is necessary, however, to point out once again that the ideal critical diameter will characterize only the probability of obtaining martensite and allow for the effect of the alloying elements and carbon precisely in this direction. The maximum value of martensite hardness, on the other hand, is determined only by the carbon. Thus, it is scarcely admissible to establish

coefficients permitting conversion of the alloying elements to the so-called "equivalent amount of carbon", as certain foreign investigators attempt to do. It is precisely this circumstance which embodies one of the fundamental differences between low alloy steels and carbon steel of equal strength: by lowering the carbon content to the minimum and obtaining the required strength through introduction of alloying elements, we obtain a steel possessing good weldability.

Lowering of the hardness in the seam zone caused by coagulation of the disperse phase at temperatures far above the tempering temperature in strengthening treatment is possible in steel which has been strengthened by precipitation hardening prior to welding. Such a case is illustrated in Figure 241 for a steel alloyed with copper the hardness of which was greatly increased by quenching and tempering before welding. For this reason, the precipitation hardening effect may be utilized for strengthening steel of which welded structures are manufactured, only when the coagulation rate of the strengthening phase is low and the structure permits conducting welding after normalizing and temper hardening after welding. The stresses in the seam and seam zone will also be decreased with such a sequence of operations.

Another circumstance involving deterioration of the properties in the seam zone is, as mentioned above, coarsening of the grain. In welding the temperature in the seam zone reaches 1400° , in consequence of which the grain is able to grow in dimensions far greater than those found in determination of the grain size number, even though the period for grain growth in welding may prove short. As is known, even in surface induction heating, as has been established, for example by K. A. Kalyshev and N. V. V'yal' [398], as well as by I. K. Zidin [246], a high heating rate limits growth of the grain, but the latter coarsens nevertheless; it is possible that this takes place to a certain extent in the cooling process. In welding, on the other hand, the conditions are even more favorable for coarsening of the grain, since in this

case not only is the initial heating higher, but as a result, even upon cooling the weld seam and the seam zone pass through a region of higher temperatures than does the layer heated for heat treatment.

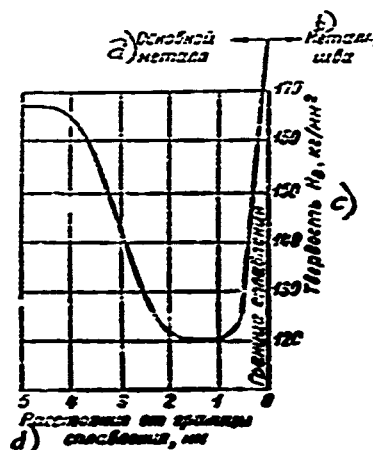


Figure 241. Lowering of hardness in seam zone of precipitation hardening steel with 0.09% C and 1.25% Cu through coagulation of hardening phase (K. V. Petran').

(a) base metal; (b) seam metal; (c) hardness H_v , kg/mm^2 ; (d) distance from fusion boundary, mm.

Since the large grain not only acts in the same direction as the alloying elements, increasing the hardenability, but also of itself increases the tendency of the steel to brittle failure, the effect of the alloying element on austenite grain growth must be of vital significance for the results of welding. Consequently, such elements as molybdenum, vanadium, and titanium, by impeding growth of the austenite grain, must from this standpoint have a positive effect on the weldability of steel. A similar effect should be exerted by deoxidation of steel by aluminum and/or titanium. Such a nature of the effect of these elements is, in fact, observed in the vast majority of cases.

However, it is necessary to add the observation that at the temperatures to which steel is heated in the welding process, even the stable phases change to solution, so that the grain would have to grow vigorously even in steels

containing intensely carbide forming elements or having a "fine grain" due to reoxidation by aluminum. Apparently, the insufficient time also plays a very important positive part because the carbides or other phases impeding grain growth do not succeed in dissolving completely. If we continue the analogy, which seems to be appropriate for us, with electric induction heating, it is of interest to cite here the data of I. M. Kikin who established by experiment [246] that in induction heating, in contrast to conventional heating, the stabler carbides (tungsten and molybdenum carbides in his experiments) dissociate even more vigorously than certain less stable ones (chromium carbides in his experiments), but with acceleration of the heating the temperature of full solution of the carbides rises.

The effect of the alloying elements on residual stresses and the danger of appearance of cold cracks is not limited entirely to their effect on the hardenability of steel and grain growth. In particular, lowering of the martensite point by the alloying elements contributes quite a bit to intensification of the stresses and to the occurrence of cracks. And since the martensitic point is lowered to the greatest extent by carbon, it is necessary for this reason as well that welding steel contain the minimum amount of it.

With the short duration of weld heating, the carbide solution rate makes itself felt to such an extent that the initial structure of the steel in the sense of dispersion of the carbides appreciably affects the position of the martensite point. While the carbides are highly dispersed in the initial structure, they dissolve more fully in weld heating. The more highly concentrated austenite obtained as a result of this is transformed into martensite (in zones with a sufficiently high cooling rate) at a lower temperature, and the danger of crack formation increases.

While in the seam zone non-martensitic products of austenite decomposition are obtained upon cooling, it is generally held that the higher the subcritical temperature at which they form, the smaller will be the stresses

occurring in the process and the danger of crack formation. Consequently, the most favorable must be transformation of the austenite in the pearlite region. However, it has recently been demonstrated [662] that even in the case of transformation of austenite in the intermediate region, in the 500 to 400° range, the weld stresses and danger of crack formation decreases, since the yield point at these temperatures is low and the stresses due to volume changes relax. Moreover, the volume changes in intermediate transformation are smaller and develop more slowly than in martensitic transformation. Hence steels in which intermediate austenite transformation occurs in the seam zone during rapid cooling should possess good weldability.

The lowering of the martensite point, just as lowering of the temperature of non-martensitic decomposition of the austenite, in its turn also intensifies the harmful effect of the hydrogen entering the seam zone from the filler metal. The mechanism of crack formation under the influence of the hydrogen is apparently the same in this case as upon the formation of flakes. Hence, in accordance with what was said in the chapter on flakes, the hydrogen will be more readily removed from the seam zone of the welded joint and the danger of crack formation in this case will be the less, the higher is the temperature of the $\gamma \rightarrow \alpha$ transformation.

The elements contained in the steel also have a substantial effect on the danger of occurrence of hot cracks (which usually appear at temperatures above that of the beginning of austenite decomposition). According to research by N. N. Prokhorov [652], the "technological strength" of the filler metal decreases with increase in the carbon, sulphur, oxygen, silicon, copper, and nickel content of the base metal. In steels alloyed with manganese, chromium, and molybdenum, on the other hand, a higher technological strength of the filler metal is observed. The greatest negative effect is exerted by nickel, for which reason, in the opinion of N. N. Prokhorov, steels alloyed with nickel alone must not be recommended for welded structures. The harmful effect

of carbon, sulphur, copper, and nickel on the technological strength of the filler metal may be compensated by alloying the latter (through coating) with chromium, manganese, and vanadium.

Thus, for low-alloy structural steel, which must possess various properties simultaneously: strength, corrosion resistance, weldability, etc., the selection of alloying elements is relatively limited. The alloying possibilities mentioned above are narrowed even further by requirements of a technological, and particularly economic, nature. The high cost of certain elements and the inadequate raw material reserves for their production render it inexpedient, or expedient only to a limited extent, to use them in low-alloy steels of high strength.

IX. ALLOYING OF HEAT RESISTANT AND THERMALLY STABLE STEEL

1. BASIC CHARACTERISTICS¹

Steels and alloys intended for the manufacture of parts operating under load at elevated and high temperatures for a more or less prolonged period are discussed in this chapter. The development of such steels, and simultaneously the procedures for testing their special properties, has been proceeding very intensively over the span of the last 25 to 30 years, in connection with the development of steam power plants, steam and gas turbines, ammonia synthesizing apparatus, petroleum refining equipment, jet materiel, etc., operating at high and ever rising temperatures and pressures. We shall henceforth refer to steels which possess a high resistance to plastic deformation and failure at operating temperatures up to 500-550° as thermally stable, and to steels capable of resisting plastic deformation and failure at higher operating temperatures as heatproof. Steels which possess high resistance to gas corrosion or scaling at high temperatures will be referred to as corrosion-resistant. Finally, we shall term heat-resistant those steels which simultaneously possess resistance to gas corrosion and a high resistance to plastic deformation and failure at high temperatures².

The basic requirements which may be made, separately or simultaneously, of heat-resistant and thermally stable steels, depending on the duty conditions of the machine part are: (1) strength, which is characterized by the yield point or tensile strength, in brief tension tests at an elevated or high operating temperature; (2) creep resistance; (3) stress-to-rupture strength,

¹For further details about the basic characteristics of heatproof and thermally stable steels and the methods of determining these characteristics, see the work of A. M. Borzdyka [710] and Ya. S. Gintsburg [731].

²According to GOST 5652-51, heat resistant, thermally stable, and heatproof steels proper are combined under the common designation "heatproof", and steels resisting gas corrosion at high temperatures (heat-proof steels) are termed "scale-resistant".

i. e., the amount of stress which leads to breakdown of material under prolonged application of load at the operating temperature; (4) low notch sensitivity in creep rupture; (5) fatigue strength at the operating temperature; (6) stability of the structure and properties under prolonged exposure to temperature and load; (7) resistance to relaxation; (8) heat-resistance; (9) resistance to corrosion; (10) resistance to erosion; (11) resistance to thermal fatigue; (12) capability of damping, or high logarithmic decrement of vibrations; (13) a definite modulus of elasticity; (14) definite physical properties: a low thermal expansion coefficient, high thermal conductivity and temperature diffusivity, etc.

The strength and plasticity at high temperatures, as determined by a 20 to 30-minute stress rupture test, play a subordinate part. However, these characteristics acquire independent importance for parts which are subjected to the action of high temperatures under load for a very brief period, or of low temperatures at which creep has practically no effect as yet. At temperatures above 350-400°, no yield strength offset is generally to be detected in the stress-strain diagram. In these cases yield strength is determined, i. e., the stress corresponding to the specified permanent elongation, most frequently 0.2%. The yield strength is plotted against the temperature on one diagram with the creep characteristics for the same steel, in order to determine the temperature below which calculations may be conducted on the basis of the yield point value. This temperature, all other conditions being equal, depends on the permissible creep rate or total strain. An example of such a plot is shown in Figure 301 [427] for pearlitic 5% chromium-molybdenum steel and for austenitic steel of the OKh18N9 type. It is to be seen from the diagram that up to ~ 425° for the first steel and up to ~ 600° for the second, the value of the stresses corresponding to a creep rate of 0.1% per 1000 hours exceeds the yield point $\sigma_{0.2}$; consequently, up to the temperatures indicated the latter may be used as a basis for calculations

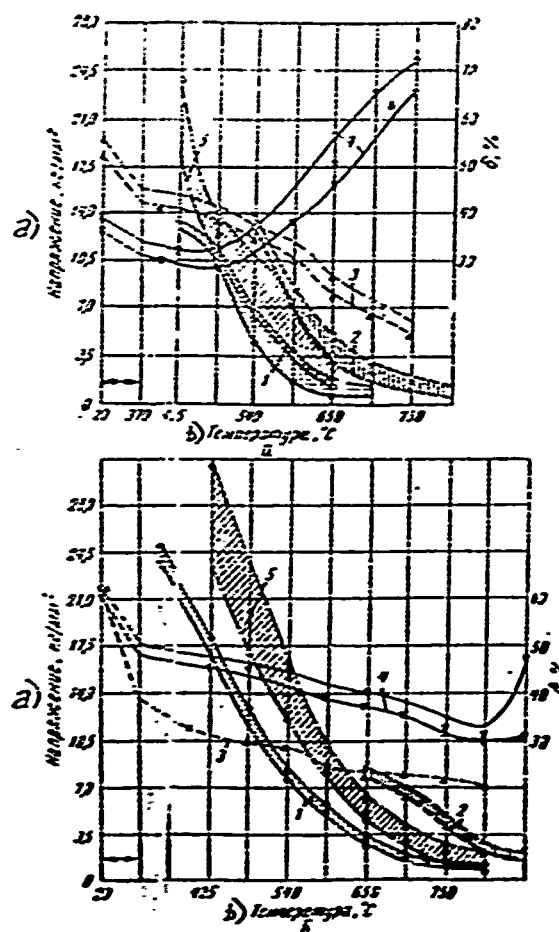


Figure 301. Change in mechanical properties of pearlitic (a) and austenitic (b) steel with temperature:
 1 - 0.01% creep; 2 - 1000 hours to failure;
 3 - $\sigma_{0.2}$; 4 - elongation δ at failure; 5 - 0.1% creep.
 (a) stress, kg/mm^2 ; (b) temperature, $^{\circ}\text{C}$.

for these steels.

If the steel is intended for service under stress over a long period, to characterize its strength at high temperatures it is necessary to know either the creep resistance or the value of the stress which leads to failure under lasting load, but most frequently both. The creep resistance is of decisive

importance in the evaluation of a steel whenever negligible total strain is envisaged for a part over a long period of service, such as 1% in several years. If, on the other hand, considerable strain is envisaged for the part and only failure must be eliminated, the magnitude of the stress which leads to failure under lasting action of load may prove decisive. This characteristic, as proposed by A. M. Borzdyka, is designated long-term strength (creep rupture).

It has been found by a number of investigators that the stress versus time to failure graph plotted in double logarithmic coordinates is a straight line (Fig. 302a) whose angle of inclination to the X-axis depends on the test temperature (Fig. 302b). Hence it is possible in principle, by extrapolating these lines, usually brought by experiment to 1500-3000 hours, to find the long-term strength, which corresponds to periods of tension of 10,000 and 100,000 hours¹. However, only the long-term strength values obtained by experiment may be regarded as fully reliable, since additional processes such as oxidation, corrosion, structural changes, etc., which favor intercrystalline brittle failure, may have an intense effect in the event of more protracted periods; this results in a break in the stress-time line (Fig. 302c). Consequently, bringing the specimen to failure also permits revealing processes of "embrittlement" of the material, which in a number of cases sharply reduce its plasticity characteristics -- elongation and contraction.

The primary creep curve, which depicts the increase in permanent set with time at constant values of stress and temperature, is shown diagrammatically in Figure 303. Hence the creep rate $\dot{\epsilon}$ on the rectilinear segment of the curve bc is determined. The rate $\dot{\epsilon}_c$ increases with increase in the test temperature and stress. In many instances the total deformation of a specimen in a speci-

¹For a proposed more reliable extrapolation method, see I. A. Odling and V. S. Sb. Instituta metallurgii AN SSSR "Issledovaniya po zharoprochnym splavam" [Symposium of the Institute of Metallurgy of the Academy of Sciences of the USSR "Research on Heatproof alloys"], Publishing Office of the Academy of Sciences of the USSR, p. 52, 1956.

fixed period of time is of importance. Such experimental curves having been plotted at constant temperature and various stress values, the creep limit is determined, which characterizes quantitatively the resistance of the steel to creep at a given temperature. In this case the theoretical or physical creep itself, which represents the maximum stress at which the creep rate equals zero, is very seldom determined. The resistance of steel to creep is usually characterized by an arbitrary creep strength, which is the adopted unit stress responsible either for a specified creep rate v_c on a rectilinear segment of the curve in Figure 303 (σ_c), or for a specified total deformation in the course of a definite period of time (σ'_c). From the curve in Figure 303 it is also possible to determine the elongation, which corresponds to the bending point c.

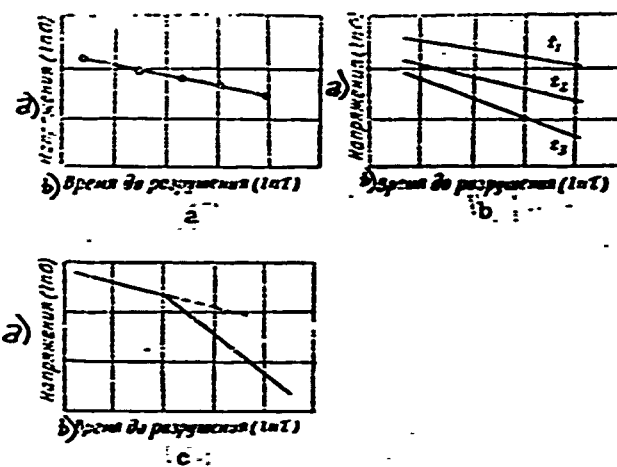


Figure 302. Breakdown stress versus duration of its action:
a and c - at constant temperature; b - at various temperatures;
(a) stress ($\ln \sigma$); (b) time to failure ($\ln \tau$).

Combined diagrams are frequently plotted for the long-term strength and creep. An example of such a diagram in logarithmic coordinates is shown in Figure 304 for chrome-molybdenum steel. The top line represents the relationship of stress to time to breakdown. Curves of creep at various loads are plotted in the lower part of Figure 304. The values of the time in the course

of which a total creep of 1% at 480°C is reached have been taken from these curves; the relationship of this time to the stress gives the second diagram from the top (also a straight line). Finally, the extreme points of the creep curves denote the values of ultimate elongation, which decreases with increase in the duration of action of the load. By connecting the points corresponding

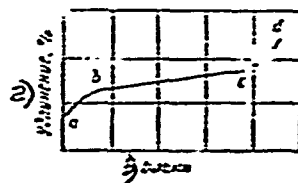


Figure 303. Diagram of primary creep curve.
 $t^0 = \text{const}; \sigma = \text{const}.$
 (a) elongation, %; (b) time.

to the values of ultimate elongation by a line and extrapolating the latter to 100,000 hours, we find that for the steel in question the ultimate elongation drops from $\sim 20\%$ in 1000 hours to $\sim 5\%$ in 100,000 hours. By extrapolating the upper two lines, we find the long-term strength σ_D corresponding to a time of 100,000 hours and the stress σ_c causing a total creep of 1% in 100,000 hours. The ratio of these stresses $\frac{\sigma_D}{\sigma_c}$ gives the margin of safety at the given temperature for the steel in which we are interested. The reliability of the material in service is also frequently characterized by the ratio $\frac{\sigma_D}{\sigma_c}$.

Numerous accelerated methods of determining the characteristics of steel's resistance to creep, proposed and used to a certain extent thus far, chiefly by foreign investigators, may quite rightly be regarded as not sufficiently accurate [cf. 710]. In addition, the accelerated test methods, as has already been pointed out, do not take into account processes which develop very slowly in the steel, and these processes may have serious consequences. Even the long-term hardness method, very tempting because of its rapidity, is no exception in this respect. Nevertheless, in the laboratory testing of heat-proof alloys A. A. Bochvar considers it possible to make a tentative qualitative selection of experimental alloys on the basis of the results of measure-

ment of their hardness. However, alloys possessing high long-term strength values still cannot be recommended as heatproof alloys without a check by the tension method, since the long-term hardness is not affected by certain features of the structural condition of the alloys, primarily the condition of the grain boundaries [44; cf. also 710]. Use is also made for tentative qualitative selection of experimental alloys of the centrifugal bend test method developed by I. I. Kornilov [360].

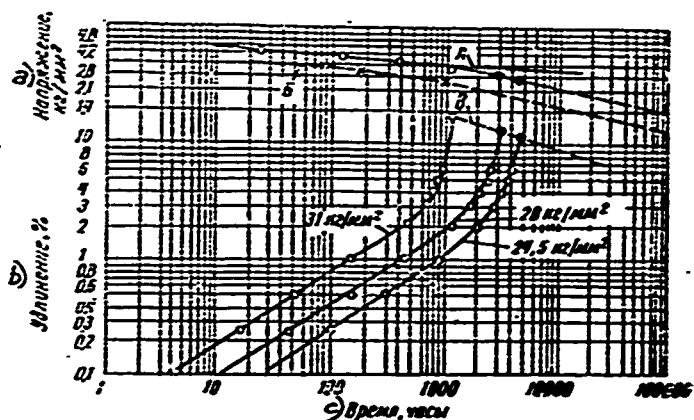


Figure 304. Combined diagram (of long-term strength and creep) in logarithmic coordinates for a chromium-nickel-molybdenum steel with 0.42% C, 0.69% Mn, 0.25% Si, 0.72% Cr, 1.84% Ni, 0.34% Mo, quenched from 950° and tempered at 675° (L. Ya. Liberman):
 O - intercrystalline fracture; A - failure at 480°; B - 1% creep at 480°; C - elongation at failure;
 (a) stress, kg/mm²; (b) elongation, %;
 (c) time, hours.

It should be noted that even in the case of testing by direct methods and sufficient length of the test period, the values determined of the long-term ultimate strength of the same alloy may vary over a wide range, not only in different countries, but also in one laboratory with specimens from different melts and even from one melt [626 et al.]. These fluctuations are also affected by the error of the test itself and the high sensitivity of the characteristics determined to the melting procedure, further treatment of the

ingots and blanks, action by the medium, and random defects which may play the part of notches, etc. This must be taken into account particularly when comparing results obtained by different investigators.

Relaxation consists in the circumstance that the elastic strain of a part caused by a definite stress changes to plastic strain, this leading to spontaneous lowering of the stress. This effect is of particular importance for a steel from which fastening parts such as bolts are manufactured, since when the stress is lowered, the elastic shortening ensuring firmness of the corresponding connection is relieved. Relaxation has much in common with creep. Hence both effects are occasionally considered identical, and it is even proposed that relaxation be used as a method of testing creep and vice versa. The rate of increase in plastic deformation in relaxation is considered by some as equal to the creep rate, while others contest this thesis. However, this is a special question. Insofar as our topic is concerned it is necessary to note the circumstance that far from all alloys which resist creep well also possess high relaxation characteristics [cf. 710].

The fatigue strength at high temperatures is an important characteristic for parts in service under alternating stresses. At high temperatures the right-hand segment of the fatigue curve, as may be seen from the schematic in Figure 305, becomes sloping instead of horizontal. In consequence of this, the fatigue limit decreases with increase in the number of cycles; moreover, its decrease is the greater, the higher is the operating temperature. Its value should thus be determined and indicated for a specified number of reversals, and a fairly high number should be adopted. The high-temperature fatigue limit in smooth specimens is usually higher than the limits of creep and long-term strength, with the length of the test period roughly identical [710]. In this case, consequently, failure ensues earlier under the effect of creep than under the effect of fatigue. This is apparently due to the fact that the fatigue effects are determined chiefly by intragranular processes

and creep chiefly by processes in the grain boundary layer which is a "weaker spot" at high temperatures.

Directly allied with the problem of fatigue is that of cyclic ductility (the capability of steel of absorbing irreversibly the energy of vibrations; it is characterized quantitatively by a hysteresis loop). Although the significance of the cyclic ductility of steel for the service of parts has not yet been definitely ascertained (with the exception of resonance conditions), it may nevertheless be assumed that of two steels having an identical fatigue limit, the one with the higher cyclic ductility will be the better one¹.

Notch sensitivity is usually determined as the ratio of the values of the long-term ultimate strength of a notched specimen and of a smooth specimen. It must be borne in mind here that determination of these characteristics by extrapolation may lead to erroneous conclusions, since in certain materials notch sensitivity is intensified in the course of time and the lines denoting the dependence of the breaking stress on the length of the test period (Fig. 302) for a smooth and a notched specimen may intersect. Many highly heatproof alloys are sensitive to skewing, and their long-term strength decreases greatly even in the event of a slight skew angle of the specimen (1.5° ; cf. [627]).

A highly important characteristic of thermally stable and heatproof steels is the stability of their structure and properties under the prolonged action of temperature and load. Instability may be the result of various processes taking place in the steel at elevated or high operating temperatures. Certain of them are accelerated under the action of a load. Such processes include, for example in pearlitic steels, graphitization, spheroidizing of carbides, change in the composition of the carbide phase and solid solution due to diffusive redistribution of the alloying elements between them, and

¹For further details concerning cyclic ductility and its significance, cf. [547].

processes causing thermal brittleness. In high-chromium steels these are processes which result in the so-called 475-degree brittleness, and in austenitic steels, precipitation from the solid solution of carbides, nitrides, metallic compounds, formation of the α -phase, σ phase, and other phases. The extent of instability of the steel is established by prolonged holding of specimens without load or under load (at the same time that the basic characteristics are determined) in the temperature range under consideration and subsequent determination of its structure and properties.

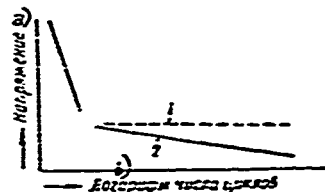


Figure 305. Diagram of fatigue curves at room (1) and high (2) temperature.
(a) stress; (b) logarithm of number of cycles.

Of the physical properties, together with high thermal conductivity and temperature diffusivity, a thermally stable and heatproof steel must for many areas of application possess a low thermal expansion coefficient. For example, for turbine disks in the event of a low thermal expansion of the steel, not only is there less change in the clearance at different temperature service conditions, but there is also a decrease in the temperature stresses occurring in them. A low thermal expansion coefficient, together with the other properties, is of no less importance for increasing the resistance of the alloys to the occurrence of thermal fatigue cracks [cf. 732 et al.]. A number of articles which are subjected to abrupt temperature changes in service are frequently rendered unserviceable for precisely this reason.

2. THE ROLE OF ALLOYING ELEMENTS IN HEAT-RESISTANT AND THERMALLY STABLE STEELS.

The effect of alloying elements on the resistance of steel to plastic deformation and failure at high temperatures and on its corrosion-resistance (resistance to scaling) obeys various laws. Hence we shall discuss separately their effect in both principal directions.

A. THE ROLE OF ALLOYING AND OTHER FACTORS IN INCREASING THE CORROSION-RESISTANCE AND THERMAL STABILITY OF STEEL.

General Principles

The resistance of alloys to plastic deformation and failure at high temperatures is determined basically by the same physical and physico-chemical factors as at room temperature. These factors are the type (the interrelation of the various types) and strength of the interatomic bond and the structure of the alloy.

In particular, there are at the present time many grounds for assuming that neither lowering of the rupture stress under the prolonged action of load (long-term strength) nor creep constitute phenomena peculiar only to high operating temperatures. In a number of projects with the most varied materials, both non-metallic and metallic, lowering of the strength at room temperature with increase in the period of action of the load has been established. It has been demonstrated [510] that the dependence of the time to failure τ on stress in semi-logarithmic coordinates is depicted with sufficient accuracy by a straight line and described by the statement of equality¹ $\tau = Ae^{-d\sigma}$, where A and d are constants, d is the angle of slope of the

¹The experiments of S. N. Zhurkov and E. Ye. Tomashevskiy [510] have shown that upon change in the duration of the test (durability) by even 10 orders, this expression is confirmed better for both non-metals and metals than the expression $\tau = B\sigma^{-n}$ usually adopted, but that it is a particular case (for a definite range of values of σ), of a more general principle which has not as yet been established.

line. It may be seen for polystyrene (polymer of styrolene) from Figure 306 [510] that with decrease in temperature the time dependence of strength varies regularly and at sufficiently low temperatures may become difficult of detection. The temperature dependence of the time is described by the expression

$$\tau = B e^{\frac{E}{kT}},$$

where B is a constant depending on the nature of the material and E represents the activation energy of the process leading to failure, which energy decreases with increase in the stress.

As we have already noted ([Russian] p. 209), these data permit the assumption that the process of breakdown proceeds via gradual local rupture of the interatomic bonds; this rupture is possible because of the inhomogeneity of the material and distribution of the stresses, fluctuations of the energy of the thermal vibrations of the atoms and strength of the interatomic bond, and in the case of metals also as a result of slips in plastic deformation. This is attested to to a certain extent by the static distribution found by S. N. Zhurkov and others [510] of the durability or longevity, i. e., the time to failure, and the irreversibility of the process, which consists in the circumstance that the total durability scarcely changes in the event of intermediate removal of load and protracted "rest" of the specimens.

If we proceed on the basis of this reasoning, we may assume that the "activation" energy E is directly related to the bonding energy, in consequence of which it decreases with increase in stress. Hence the time dependence of the strength with respect to quantity must be determined in approximation by the homologous temperature. This temperature for polystyrene -- 194° , at which the strength still decreases faintly with increase in the period of load application (Fig. 306) -- is greater than $0.2T_{\text{soft}}$ (the absolute softening point). For steel, on the other hand, room temperature is still

less than $0.2T_{\text{melt}}$, for which reason an appreciable time dependence of strength is observed here only at elevated and high temperatures.

It is obvious that the creep rate is also determined by the homologous temperature. In such metals as lead, for which room temperature corresponds to $\sim 0.5T_{\text{melt}}$, the creep occurs even at this temperature at a considerable rate under low stress. In the case of stresses exceeding the yield point, on the other hand, considerable creep has been observed at room temperature in steels as well in a number of studies.

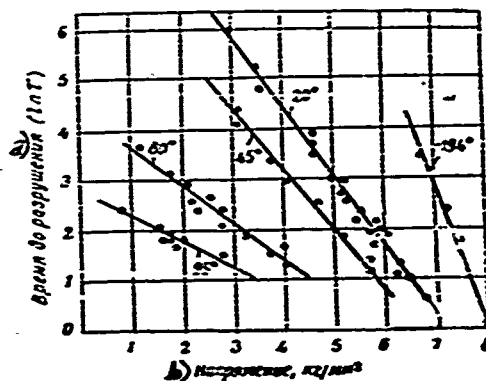


Figure 306. Time to failure versus stress at various temperatures for polystyrene.
(a) time to failure ($\ln \tau$); (b) stress, kg/cm^2 .

However, the features which are contributed by high temperature and which will manifest themselves the more the longer must the part manufactured from the alloy be in service are of enormous importance for the heat-resistance of metals and metal alloys.

The mechanism of plastic deformation, and hence also that of creep, may change at a high temperature. Many Soviet and foreign investigators have demonstrated by experiment or have suggested that plastic deformation is accomplished by various mechanisms [cf. 472, 828, et al.], which are usually subdivided into three groups [715]. Examining it from a more general standpoint, we may deal with two basic groups of processes, those of shear and diffusion.

According to the diffusion mechanism, as was suggested long ago, deformation comes about through plastic flow, as in amorphous bodies. The relation between the course of deformation in accordance with the various mechanisms and creep is still far from being established, although there is no want of assumptions relative to this question [cf. 710, 715, 829, et al.]. The experimental data are highly contradictory. Even the investigators who hold that the form of the creep curve in the final analysis depicts the difference of the effects of softening and strengthening frequently draw contradictory conclusions on the question of the effect of a given process on strengthening and of the reason for such an effect.

It may nevertheless be assumed that one or another plasticity mechanism will predominate, depending on the operating temperature, magnitude of stress, and duration of action of load. At temperatures below $\sim 0.1 T_{\text{melt}}$, shear mechanisms predominate. At temperatures above 0.3 to 0.5 T_{melt} , when the diffusion rate becomes considerable, diffusion mechanisms of plasticity begin to operate, and even to predominate at definite stresses. The part played by the diffusion mechanisms of plasticity will be the greater, as compared to the shear mechanisms, the smaller are the stress and rate of plastic deformation (creep), since considerable time is required for the development of diffusion processes. In particular it has been demonstrated [716] that under conditions of relatively small stresses and low creep rate, the mechanism of grain displacement predominates.

In the boundary (intercrystalline) layer, diffusion proceeds at a much higher rate than within the grain. Hence in the event of predominance of diffusion mechanisms of plasticity, plastic deformation develops chiefly in the boundary layer of the grain, and primarily the grain boundaries must be strengthened in order to increase the resistance of the alloy to creep. The differing role of the grain boundaries under different conditions of deformation has been confirmed by experiment in a number of studies, particularly with specimens of aluminum, consisting of monocrystals in section and several

crystals in length [711], with specimens of carbon steel heated while under load in vacuo [712], etc.

The main feature of the effect of high temperature on the long-term strength of metals and alloys consists in the presence of two branches on the straight line of the logarithmic stress - time-creep diagram, i. e., a break in the line (cf. Figs. 302c and 304) which occurs after a certain stress period, which differs for different metals¹. In saying this, we thus proceed on the basis of the probability indicated above that in general lowering of strength with increase in the duration of action of load is a principle inherent in all materials even at normal temperature, while raising the temperature only renders it more pronounced (Fig. 306). Hence, the left-hand branch of the diagram, even at an elevated temperature, may be ascribed to gradual local rupture of the interatomic bonds.

The breakdown along the right-hand branch of the logarithmic line is intercrystalline in the vast majority of cases and upon microscopic inspection appears as the result of generation and development of cracks. Hence the hypothesis advanced by S. T. Kishkin [cf. 511, 622], according to which the generation and development of cracks are the cause of lowering of the strength and plasticity of alloys working under load at high temperatures, appears more certain than other hypotheses, regardless of what causes the occurrence of the initial cracks. It has also been demonstrated [718] that allowance for susceptibility to damage, i. e., for the characteristic opposite to the resistance of an alloy to the occurrence of initial cracks, at least in the case of intercrystalline failure in the process of long application of load at high temperature, may result in a qualitative arrangement of the materials being evaluated other than that based solely on the allowance for their resistance to total breakdown.

¹At a very high homologous temperature, it is possible that a break may not be detected in the event of short duration of load application and a conventional experiment.

Since intercrystalline failure along the right-hand branch of the line in Figure 302c occurs at relatively low stresses and long period of load application, the causes of the initial cracks are usually sought in this case in diffusion processes. The most widespread hypotheses are based on the "hole" theory of diffusion developed by Ya. I. Frankel'. The authors of these hypotheses hold that the cracks are the result either of diffusion of vacancies, which are present and develop in the process of work, toward the grain boundary, where they gather in "colonies" [714] or of displacement of extant and continuously nascent "fusion foci", which are taken to mean disordered atoms, surrounding the "vacancy" toward the grain boundaries (which are more favorable regions at high temperatures, with respect to energy), where they coagulate [715].

Highly important accessory, and sometimes even decisive, causes of the origination and development of cracks, and in the final analysis brittle failure, even in the opinion of the authors of the hypotheses referred to, may be processes which occur at the operating temperature and lead to the formation on the grain boundaries of phases which lower the tear resistance. If the precipitating phase is situated primarily inside the grain along the slip planes, as was observed, for example, in a nickel alloy while being tested for fatigue at 750° [717], it also facilitates transcrystalline failure.

In our opinion, however, if we proceed on the basis of the hypotheses concerning the decisive role of diffusion of vacancies, it is difficult to explain why heating at the same temperature without load, even for a much longer period of time, fails to result in diffusion of the vacancies toward the grain boundaries, where, upon subsequent application of load, they should immediately manifest themselves as cracks. On the other hand, intercrystalline failure is observed in the main even at temperatures at which diffusion processes can play no part, or at very high temperatures but in a period so short that it must be insufficient for diffusion of the vacancies and their gathering in

colonies.

We suggest that a prominent part is played in the resistance of metals to plastic deformation and failure at high, as well as at medium and low, temperatures by the partially-ordered structure of the boundary of the grains, in whose central portion it approaches the "amorphous" structure. In consequence of this, as was suggested as long ago as the first quarter of this century [cf. 829] and discussed in greater detail on [Russian] pages 72 and 215, the basic properties of amorphous bodies must to a large extent be inherent in it.

The following properties typical of amorphous materials are of interest insofar as they apply to heatproof alloys.

1. The high dependence on time of their capability of deformation. Deformation in them is accomplished through viscous flow and occurs under very small loads, even their own weight, if the loads act over a fairly lengthy period of time. It is of interest to note that Ya. I. Frenkel' [618] admitted the possibility of existence of viscous flow even in crystals in the event of extremely small spalling forces and a very long period of their action.

2. A much more abrupt change in their properties with change in temperature than in the case of crystalline materials. In particular, the capability of deformation by means of viscous flow is greatly increased, while the effect on it of the time factor decreases sharply with rise in temperature, and at temperatures near the end of softening, the effect of time is difficult to detect.

It thus seems to us that the length of the period during which the metal is under load plays a decisive part here, in connection with the first feature of the boundary layer of the grains as an "amorphous" substance. Slip mechanisms of plastic deformation in the grain predominate along the left-hand branch of the line in Figure 302c, i.e., with a relatively short period of load action (this period may be the longer, the lower is the temperature). Hence

failure occurs with time, for the general reasons referred to above, through gradual local rupture of the interatomic bonds and is intracrystalline in nature. The creep rate in this case decreases with time due to the predominance of hardening over softening, as in ordinary "semi-hardening". With decrease in the stress and increase in the period of its application, deformation of the boundary layers of the grains by viscous flow begin to predominate. This leads to gradual "separation" of the grains and finally to tough fracture, but of the boundary layers, not the grains. The grains themselves are scarcely deformed at all or undergo slight deformation in this case, while the decisive portion of the final deformation of the specimen is the result of separation of the grains. The creep, consequently, should proceed at an increasing rate in the second stage and pass to the third stage relatively early, since the area of the boundary layer decreases with time (something of the nature of a "neck" is formed), and the true stress rises, as is observed for example upon the elongation of a locally heated glass stick or plate. It is to be seen from the schematic in Figure 107 that the separation of the grains must also be accompanied by displacement of the latter along the bc boundaries, and both separation and displacement must proceed over broken planes. And it is this, apparently, which is the so-called intercrystalline plasticity, classified by I. A. Odling [715] among the peripheral processes of plastic deformation and, as has been demonstrated in certain works [716], playing the leading role in stresses causing low creep rates.

The authors of the hypotheses of the decisive role of vacancy diffusion cite as highly important proof of them [cf. 714] the closeness of the activation energy values for failure processes (or for the steady creep stage) and self-diffusion in intercrystalline failure. Thus, for example, for aluminum the activation energy of failure is about 40 kcal/mole, and the activation energy of self-diffusion about 39 kcal/mole; for platinum they are 70 and 75 kcal/mole respectively. We, on the other hand, are inclined to see confirmation

of the failure mechanism suggested by us in the closeness, established by experiment for relatively pure metals [cf. 830 et al.], of the values of the activation energy for breakdown and creep in the event of intercrystalline failure at high temperatures. The point is that in amorphous bodies, which one may to a large extent consider the central portions and boundary layers of grains of metals to be, the physical nature of breakdown and plastic flow is fundamentally the same. Hence the values of activation energy for breakdown and creep, determined under conditions in which both processes occur chiefly due to viscous flow of the boundary layer, must be close as well. In the case of intracrystalline breakdown, however, when plastic deformation results chiefly from slip processes, the activation energy for creep must be much smaller than that for breakdown. It is to be seen from Table 86, taken from the work of S. N. Zhurkov and T. P. Sanfirova [510] and pertaining to relatively low temperatures, that, for example for the same materials aluminum and platinum, the activation energy for creep in this case is actually 3 to 3.5 times smaller than the activation energy for breakdown. The latter is much greater here than in the case of intercrystalline fracture, and near the sublimation energy, the basic characteristics of the bonding energy. This is quite understandable, since the bonding energy in the grain is much greater than in the boundary layer. This is confirmed, for example, by the high evaporation of the grain boundaries upon heating in vacuo, etc. As to the activation energy of self-diffusion, in both intracrystalline and intercrystalline failures all authors cite for it values found for the case of diffusion in the grain. Hence it is smaller in the case of intracrystalline breakdown than the activation energy of breakdown (Table 86), being 0.6 to 0.7 of the value of the sublimation energy, while in the case of intercrystalline breakdown it is found to be near the activation energy for breakdown and creep because the latter are smaller, although it is apparently not directly related to them.

The breakdown mechanism proposed by us at high temperatures is confirmed by many facts and, in particular, by the preliminary results published by M. G. Lozinskiy and Ye. I. Antipova [712] of direct observations (on the polished surface of specimens) of the change in the microstructure of alloys in the process of their high-temperature heating under load in vacuo. The process consisting, in our opinion, of gradual "separation" of the grains is to be seen quite distinctly in this study in the Ni + Cu alloys, and the final deformation of $\sim 5\%$, as is illustrated by the photomicrographs presented by the authors, may be ascribed almost entirely to separation of the grains.

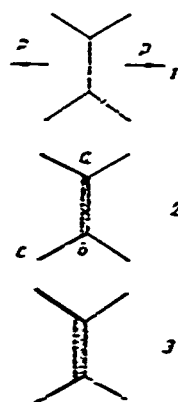


Figure 307. Diagram of "separation" of grains in different stages of loading at high temperature:
1 - initial condition;
2 - intermediate condition; and
3 - breakdown.

Shown in Figure 308 are certain microstructures from the work of Vud and Rashinger [831], in which specimens of 99.98% pure aluminum, after preliminary 8-9% cold deformation, were subjected to tension at various temperatures and at a varying rate (the slow deformation in Figure 308 corresponds to an elongation of 0.1% per hour and the rapid deformation to 10% per minute). In the authors' work these photographs are given parallel to X-ray photographs as proof of the formation of a "substructure", i. e., breaking up of the grains into blocks, cells whose dimensions increase with rise in temperature and reduction of the rate of deformation. We present these photographs of specimens which have undergone breakdown in order to point out the thickening

of the boundary layers, it being in our opinion the result of viscous flow of the latter resulting in "separation of the grains along the broken lines of the boundaries. It is to be seen from Figure 308 that separation of the grains is intensified with rise in temperature and reduction of the rate of deformation. Thus, rapid deformation at 400° (Fig. 308a) yields approximately the same picture as slow deformation at 200° (Fig. 308b). In the case of rapid deformation at 200° (Fig. 308c), on the other hand, no separation of the grains is to be seen, and slip deformation in the grain predominates.

Table 86

Metal	U_0 kcal/mole	G kcal/mole	E kcal/mole	A kcal/mole
Al	25	27.4	29.5	—
Ag	51	55	37.5	15.3
Ag	64	58	45.9	15.0
Pt	145	127	75	44.5

Note. U_0 is the activation energy for breakdown (its value obtained by extrapolation to zero stress); E that for self-diffusion (based on reference data); A that for the steady stage of creep (based on reference data); Q the sublimation energy. We have entered the E for Pt.

Localization of deformation in the boundary layer was observed in the study by E. S. Yakovleva and M. V. Yakutovich [711] mentioned above, in a specimen of 99.6% pure aluminum consisting of one crystal in section and 2 to 3 crystals in length, which failed in 10 hours under a stress of 0.144 kg/mm^2 at $550-600^{\circ}$. With silver monocrystal wires 0.1 cm in diameter and with a design length of about 4 cm, after 282.5 hours at 910° an elongation of 0.005 cm under a stress of 0.00134 kg/mm^2 and 0.001 cm under a stress of 0.00116 kg/mm^2 were obtained, while with the same polycrystalline wire under the same conditions, the elongation under a stress of 0.00128 kg/mm^2 amounted to 0.058 cm [852]. The difference may be ascribed to viscous flow of the boundary layers of the polycrystalline wire. This also apparently explains the 5 times greater decrease in density with time and earlier (~ 5 times) appearance of the third creep stage in polycrystalline aluminum at 250° and

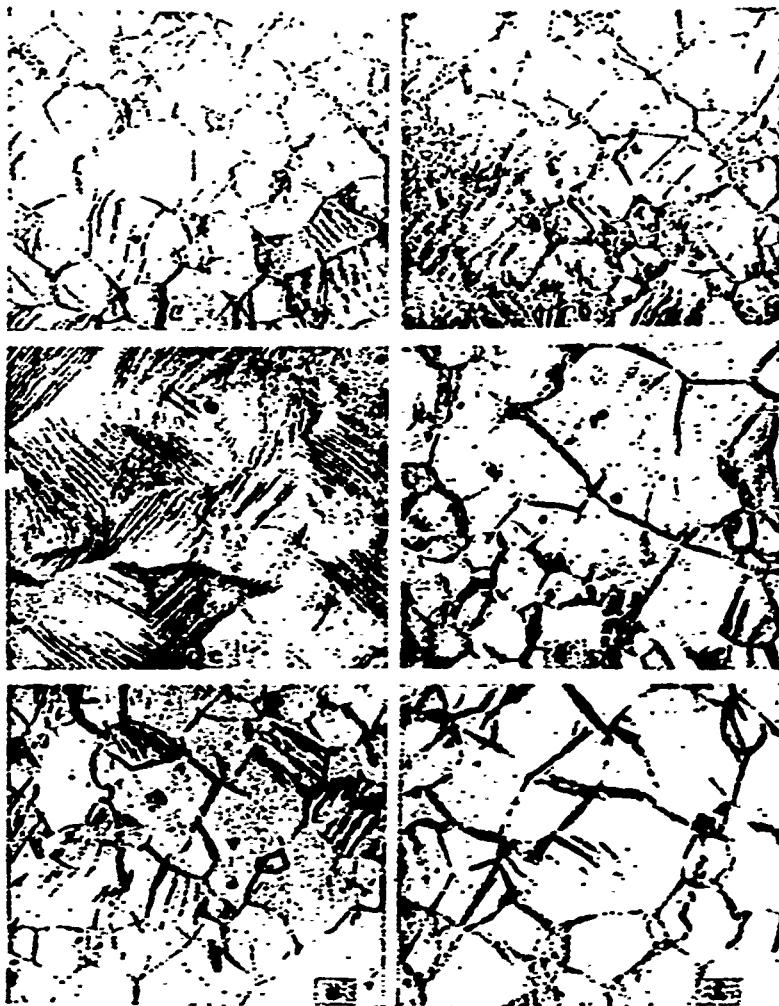


Figure 308. Microstructures of specimens of pure aluminum which have undergone breakdown, subjected to 8-9% cold deformation and then subjected to tension slowly and rapidly at various temperatures (cf. text). X 100:

a - rapid deformation at 400° ; b - slow deformation at 200° ; c - rapid deformation at 200° ; d - slow deformation at 300° ; e - rapid deformation at 350° ; f - rapid deformation at 500° .

under $\sigma = 2.2 \text{ kg/mm}^2$, observed by Khenson and Uller [cf. 622], as compared to a monocrystal under the same conditions. It is characteristic here that there was a particularly appreciable decrease in density in the third creep stage. In our opinion this is due to the circumstance that the separation of the grains only appears to be a crack on the section. In reality, however, the separation of the grains, in contrast to abrasion, is still not a crack in the initial and intermediate stages and is transformed into a crack only when tough fracture of the boundary layer begins owing to the formation of a "neck". It follows, among other things, that up to a certain stage of loading with time, it should be possible to "heal" such damages, in contrast to the damages caused by rupture of the interatomic bonds. In this apparently lies the essence of increase in plasticity and ductility owing to heat treatment of a specimen before a certain length of the period of its service is exceeded ([Russian] page 536), and to intermediate heat treatment employed at various stages of the heating of a specimen under load.

Fatigue fracture, even at high temperatures, generally, i. e. in the absence of effect by other factors, passes along the grain, apparently because the duration of that portion of the cycle during which the specimen is subjected to application of load of one sign is inadequate to cause viscous flow of the boundary layer of the grain. For this reason the breakdown process occurs here as a result of plastic deformation in accordance with slip mechanisms and of local rupture of the interatomic bonds in the grain. But at high temperatures the general time dependence of the strength has a greater effect, in consequence of which the right-hand segment of the horizontal line is transformed into a sloping straight line (Fig. 305), i. e., the "fatigue limit" is lowered with increase in the number of cycles.

With rise in (homologous) temperature, the behavior of the boundary layer of the grains is affected, in our opinion, by a second typical property of amorphous bodies, the sharp increase in their capability of plastic flow, in

consequence of which the role of the time factor is greatly reduced. Thus, at 350° rapid deformation of aluminum (Fig. 308e) leads to approximately the same separation of the grains as slow deformation at $\sim 300^{\circ}$ (Fig. 308d). Rapid deformation at 500° (Fig. 308f), and at 400° (Fig. 306a) yields a particularly sharp picture. In the work referred to above [712], the duration of load application to Ni-Cu alloys up to failure did not exceed 14 hours, but the temperature was 650° , i. e., about $0.6T_{\text{melt}}$, and the stress 6.7 kg/mm^2 . On the other hand, V. I. Danilovskaya and other [833] observed in the 30KhMA steel a retardation of relaxation in the event of preliminary creep under a stress of 20 kg/mm^2 for 25 hours at a temperature of about $0.4T_{\text{melt}}$ (500°C), while the same plastic deformation, but obtained by preliminary short-time extension at the same temperature, scarcely had an effect on the relaxation rate. This induces the authors to infer a difference between the mechanism of creep and that of ordinary plastic deformation. Apparently, in consequence of the great effect of the time factor at this temperature, in the case of creep the deformation was accumulated chiefly through viscous flow of the boundary layers of the grains. In the case of preliminary short-time extension, on the other hand, the plastic deformation was due only to a slip mechanism within the grains. Consequently, the authors apparently were dealing in reality with different mechanisms of the process.

It is to be noted in this connection that the concept of the so-called "equicohesive" temperature, above which failure is intercrystalline in nature and below which it is transcrystalline, is generally speaking, devoid of meaning. There are indications in the literature [cf. 714] that the equicohesive temperature is not constant, but rather depends on the stress and creep rate. In fact, on the one hand, in the event of a very short load application even at a very high temperature, it is possible to obtain intracrystalline fracture. Thus, for example, it was demonstrated in an old study by Dzheffris [cf. 829] that at 950° , i. e. $0.9T_{\text{melt}}$, a copper wire was tough fractured along the grain

under a stress of 1.75 kg/mm^2 in 5 seconds and exhibited a brittle failure along the grain boundaries under a stress of 0.5 kg/mm^2 in 60 seconds. On the other hand, in the event of a very long exposure to stress, it is to be expected that the failure may be intercrystalline even at moderate temperatures ($0.15-0.4T_{\text{melt}}$). It would have been possible to confirm this thesis with experimental facts as well, but we refrain from doing so, because in almost all such examples available thus far there is no certainty that additional factors responsible for a change in the condition and properties of the boundary layer, would not have been reflected thereby.

Still another highly important feature contributed by a high operating temperature lies in the fact that the tendency of the alloy to achieve thermodynamic balance may hereupon be realized, this leading in a number of cases to lowering of the alloy's resistance to creep and breakdown. Thus, for example, in alloys aged by precipitation hardening through annealing at a temperature below the operating temperature, coagulation of the strengthening phase, its reverse solution, or further precipitation of it from the supersaturated solid solution may occur in the process of service. In alloys hardened by cold working, the process of restitution or recrystallization may occur at the operating temperature. In alloys in which metastable carbides were precipitated as a result of hardening, diffusion of the elements from the solid solution to the carbide phase up to the formation of stable carbides, as well as spheroidizing of the carbides, graphitization, etc., may occur at the operating temperature. In the case of long exposure to the effect of temperature, processes -- which in certain instances are still unknown -- may take place in the solid solution itself and cause a considerable stability of the latter. The stresses created in the alloy by the effective load may intensify such processes.

The enumerated highly important features of the effect produced by high operating temperature also determine the peculiarities of the alloying

and heat treatment of heat resistant and thermally stable steels and alloys. The methods of alloying and heat treating such steels must thus vary in relation to their proposed duty, i. e., operating temperature, stress, and length of service.

Metals (alloy base) and single-phase alloys

The interatomic bond of the matrix metal must possess a high strength. For heatproof alloys, as it follows from the presumed role of the grain boundaries we have discussed, it is necessary in addition to find means which either lead to increase the order of atomic arrangement in the boundary layer or to the formation of phases with very strong interatomic bonds, or to both simultaneously. The strength of the interatomic bond may in the first rough approximation be characterized by the melting temperature. The latter for heatproof alloys is also an important independent characteristic, inasmuch as it determines the upper temperature limit which an alloy may in general withstand. But in addition, the higher the melting temperature of the alloy, the lower the homologous temperature to which a given operating temperature corresponds. Hence for service at high temperatures use is made of alloys based on iron, nickel, and cobalt, while for service at very high temperatures alloys based on chromium, molybdenum, which are even more high-melting¹ and have a greater interatomic bond strength, are being developed.

The interatomic bond strength apparently also determines chiefly the different heat-resistance of steel with an α and γ lattice. According to our assumptions (page 215), resistance to low plastic deformation, and hence to creep as well, is determined principally by the interaction of ions in the metallic bond, which interaction is the greater, the larger the number of unpaired electrons per atom, and decreases with increase in the interatomic distance. The forces of this component of the metallic bond in α iron are much greater than in γ iron (see page 34), this being evidenced by the greater

¹The high-melting point is nevertheless only a necessary, but not always sufficient, factor.

thermal expansion coefficient of the latter. The rate of diffusion and self-diffusion, on the other hand, is determined by the full strength of the metallic bond, which is greater in γ iron, as is attested to a certain extent by its greater modulus of elasticity than the α iron. Also associated with a lower rate of self-diffusion is the higher recrystallization temperature of γ iron as compared to α iron, this being of independent positive significance from the standpoint of heat-resistance. Moreover, the response of γ iron to work hardening is greater than that of α iron. Finally, the orderliness of the atomic arrangement in the grain boundary layer is also, apparently, greater for the γ iron than for the α iron, as we assume this to be evidenced by the behavior of austenitic steels upon deformation and failure in the region of moderate and low temperatures.

Hence at relatively low operating temperatures, up to $0.3 - 0.47 T_{\text{melt}}$, ferritic or pearlitic steels possess a higher creep resistance so long as slip mechanisms of plastic deformation predominate. At higher temperatures, when diffusion plasticity mechanisms begin to prevail, the austenitic steels have a greater creep resistance. Pearlitic-ferritic-martensitic steels may thus be employed as thermally stable steels. For heatproof steels and alloys, on the other hand, use should be made of austenitic steels or alloys based on other matrices with a γ lattice such as nickel and cobalt.

In alloys, the role of the interatomic bonds is in the majority of cases camouflaged by structural factors. In a more direct form, it is manifested in the solid solutions, although even in them other factors still make themselves felt, in particular distortions of the crystal lattice of the solvent by the atoms of the solute element. With one and the same solvent, the intensification of ion interaction caused by increase in the number of unpaired electrons per atom should lead to an increase, to one extent or another, of creep resistance if both slip and diffusion mechanisms of plasticity predominate.

To this may apparently be ascribed the fact that a number of highly important elements increase the creep resistance of single-phase alloys based on iron and nickel. Thus, iron, titanium, tungsten [634], aluminum, and chromium [432] increase the heat-resistance of nickel; manganese, a low content of chromium, and, to the greatest extent, molybdenum increase the creep resistance of iron. The effect of molybdenum may be seen from Figure 308 [438], in which is given the value of stress causing failure or creep at a rate of 0.1, 0.5, and 1% per 100 hours at 650°. Tungsten has the same effect on the creep resistance of iron. As it may be seen from Figure 17, in which the ionization

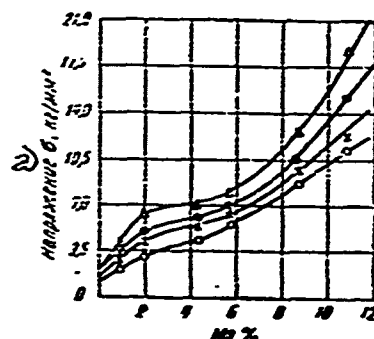


Figure 309. Effect of molybdenum on resistance of Fe-Mo alloys to failure and creep at 650°: Δ - failure; \bullet - 1% creep in 100 hours; \times - 0.5% same; \circ - 0.1% same; (a) stress σ , kg/mm²

potentials of iron and nickel when they are solvents are marked with crosses, all these elements must add an electron from the iron or nickel, increasing the number of unpaired electrons per atom in their lattice and intensifying the interaction of the ions. Increase in the strength of the interatomic bond in the nickel lattice when it is alloyed separately with chromium, aluminum, or titanium, has also been established by experiment [635]. The same is true of chromium and manganese when iron is alloyed with them. Silicon also augments the creep resistance of iron, although it reduces the strength of the interatomic bond in the latter (see [Russian] page 37). We are inclined to ascribe this circumstance, as well as the increase by silicon of the yield point of iron at room temperature (see [Russian] page 228), to the fact that it introduces into the alloy an appreciable share of the covalent bond,

the basic property of which is high resistance to plastic deformation, even at elevated temperatures.

When steel is subjected to load under conditions in which slip mechanisms of plastic deformation predominate, elevation of the recrystallization temperature by the alloying element exerts a positive effect on the creep resistance. The data of Fermann cited below, which have in the main been confirmed in later investigations [127, 438, and others], for cold working with 90% reduction may give a rough idea of the qualitative effect of certain elements in this direction.

Content of element, % (atomic)	Electrolytic Fe	4Al	2Si	2V	4Cr	4Co	4Ni	2Mo	1W
Recrystallization temperature, °C.	520	600	600	620	700	640	600	750	760

Insofar as concentration of the solid solution is concerned, it has been demonstrated in a number of studies by I. I. Kornilov and others that in both binary and more complex solid solutions, with increase in the content of the element the heat resistance, which was determined by the centrifugal method, increased until maximum solubility of the element in the alloy base was

at the given temperature and decreased upon transition to the diphasic region. The formation of the chemical compound is accompanied by singular points on the composition-heat-resistance diagram. As an example we show in Figure 310 [432] the change in heat resistance at 800°, characterized by the transverse deflection, of nickel-chromium alloys with changing chromium content, as compared to a portion of the structural diagram of the Ni - Cr system.

In reality, however, it is to be expected that the effect of the solid solution composition on the creep resistance will not be, or at any rate will far from always be, well-defined and that it must itself vary in relation to the test or service conditions of the alloy: temperature, duration, stress, as well as in relation to the distribution of the given element in the grain

and in its boundary layer. In more recent investigations, I. I. Kornilov and others [856] have also confirmed the fact that the content of the alloying element optimum from the standpoint of heat resistance, may be either greater than, or equal to, or less than its maximum solubility in the base, depending on the test temperature. The example shown in Figure 311, which is based on their investigations, may serve as an illustration. It shows the effect of titanium on the heat resistance of alloys of nickel with 20% Cr at various temperatures as against the solubility line of titanium in this base. The time to achievement of a sag of 3 and 5 mm in testing by the centrifugal method served as the characteristic of heat resistance in this case.

Increase in the strength of the interatomic bond in the solid solution lattice due to certain elements should also lead to increase in the long-term strength of the alloy due to the higher tear resistance value. We shall note only that a substantial increase in the long-term strength owing to weakening of the diffusion processes may be achieved even when the interaction of the ions is intensified. Thus, molybdenum also increases the long-term strength of iron more intensely than do other elements. According to the data of recent investigations [684], tungsten, if its content is expressed in atomic percentage, is just as effective as molybdenum, while vanadium alone, if dissolved in the iron, scarcely affects its long-term strength. On the other hand, to increase the long-term strength by increasing the tear resistance, it is necessary chiefly to strengthen the basic components of the metallic bond. This can be achieved (as with the conventional structural steels) to a lesser extent by alloying and to a much greater extent by means of the structural factor and type of lattice. It is apparent, in particular, that steels and alloys with a γ lattice for this reason also have higher values of long-term strength, and not merely those of creep resistance at a high temperature than do steels with an α lattice.

The usually observable intensification of the energy of interatomic interaction of the alloying element with the base when other elements are present in the alloy (see page 38) is responsible for the fact that it is mostly the multicomponent solid solutions that even at high temperatures, are more intensely strengthened than the binary ones. This is most sharply revealed in the case of short-term load application (see Table 87 [123]). But the interaction of the elements has an appreciable effect on both the long-term strength and the creep resistance. Thus it has been demonstrated [684] that pearlitic steel containing 1.5% Mo and 1% V simultaneously has at 650° a higher long-term strength than steel containing 5.2% Mo or 5.3% V separately. The interaction of tungsten and molybdenum in pearlitic steel augments the creep resistance, while scarcely increasing the long-term strength as against the total strength.

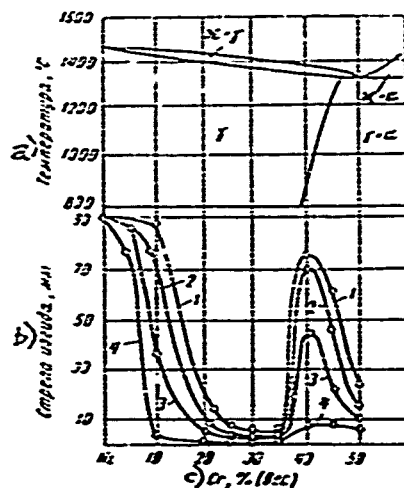


Fig. 310. Effect of chromium on the heat resistance of Ni-Cr alloys at 800°:

1 - 15 hours; 2 - 10 hours;
3 - 5 hours; 4 - 1 hour;

(a) Temperature, °C;
(b) Transverse deflection,
mm; (c) Cr, % (by weight)

To increase the creep resistance and long-term strength when the latter is exhausted in consequence of intercrystalline failure, it is extremely important to increase the strength of the interatomic bond chiefly in the boundary layer of the grain. Owing to this, the distribution of the alloying elements, as well as of the impurities between the grain and its boundary layer acquires even greater importance as it applies to heatproof alloys than it has for steels for other purposes. The role of this factor is heightened with elevation of the operating temperature and decrease in the creep rate, i.e.,

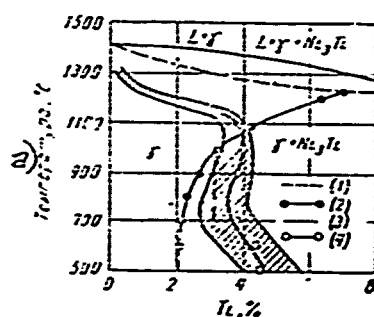


Figure 311. Effect of titanium on the fire resistance of nickel alloys with 20% Cr at various temperatures:

1 - solubility line of titanium after 24-hour anneal; 2 - maximum solubility line after protracted holding; 3 - boundaries of region of greatest heat resistance; 4 - alloys of maximum heat resistance;

(a) Temperature, °C.

Table 87

Strength of Nickel-Based Solid Solutions at Various Temperatures

Alloys	σ_b , kg/mm ² at a temperature, °C. of							
	20	300	400	500	600	700	800	900
Pure nickel	35.0	28.0	22.0	—	12.0	7.0	3.0	1.5*
Ni-Cr (20% Cr)	81.0	—	76.0	—	63.0	47.0	28.0	15.0*
Ni-Cr strengthened	2.47	—	3.5	—	5.25	6.7	9.3	10.0
Ni-Cr-Ti (20% Cr + 3% Ti)	93.0	—	95.0	90	79.0	60.0	35.0	20.0*
Ni-Cr-Ti strengthened	2.45	—	4.3	—	6.6	9.8	11.7	13.3
Ni-Cr-Ti-Al	100.0	—	102.0	—	90.0	87.0	55.0	40.0
Ni-Cr-Ti-Al strengthened	2.63	—	4.6	—	7.5	12.4	23.4	30.0

* Data obtained by extrapolation.

with decrease in the effective stress and increase in the duration of the service of the alloy under load. We have already noted on several occasions that the vast majority of the alloying elements, as many facts now force us to admit, is contained in much greater quantity in the boundary layer of the grain than in the center and volume of the grain, the difference increasing with decrease in the total percentage of the element in the alloy. Hence when several or many elements, particularly those which intensify each other's effect

on the interatomic bond strength, are introduced simultaneously into an alloy in relatively small quantities, one can obtain above all a grain boundary layer which is highly alloyed by many elements and is highly heat resistant. Practice confirms this thesis: the modern most highly heat resistant alloys checked by long-term tests and in operation have a basic mass consisting of a multicomponent solid solution.

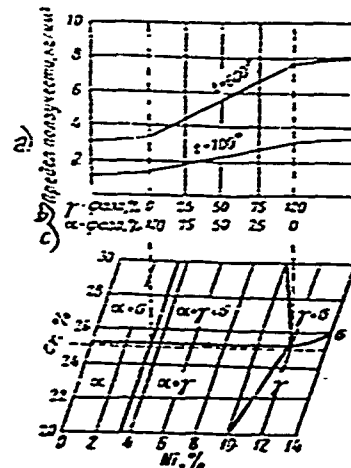


Figure 312. Change in creep resistance of iron alloy with 25% Cr upon being alloyed with nickel. (a) creep limit, kg/cm²; (b) gamma phase, %; (c) alpha phase, %.

Heterogeneous alloys

In heterogeneous alloys the structural factor may prove to be the dominant one. However, the strength of the interatomic bond plays a very important part even here, both indirectly and directly. If the second phase has less strong interatomic bonds than the basic solid solution, as its quantity in the alloy is increased, the strength of the alloy will decrease. Figure 312 [710] may serve as an example; it is to be seen from it that with increase in the nickel content in an iron alloy with 25% Cr, which increase is accompanied by rise in the quantity of the gamma phase and a corresponding decrease in the quantity of the alpha phase, the increase in the creep limit at 600 and 700° is practically rectilinear. Hence when ferritizing elements such as titanium, molybdenum, tungsten, etc., are dissolved in an austenitic base, their positive

effect on the creep resistance when contained in a certain percentage may cease and subsequently be replaced by a negative effect in consequence of the appearance of the alpha phase. This limits the use of ferritizing elements in austenitic steel to their optimum content, which may be raised if the percentage of nickel, manganese, and other elements favoring the formation of austenite and thus compensating for the effect of the additional element on the formation of the alpha phase is increased in the alloy.

The fire resistance of an alloy is also affected negatively by the presence in it of other phases which have a low interatomic bond strength and low melting temperature and tear resistance values. Such phases have a particularly harmful effect if they are situated predominantly along the grain boundaries or at the junction points of dendrites [cf. 837]. Prevention, or at least reduction, of the probability of such harmful "boundary" phases may be achieved by employing very pure burden materials, for iron and nickel based alloys -- pure with respect to their content primarily of lead, antimony, tin, and sulphur¹. An appreciable effect is gained by melting or pouring in vacuo, and particularly both. Figure 313 [cf. 838] illustrates an example of the substantial increase in the 100-hour long-term ultimate strength of a high-alloy metal based on nickel due to melting in vacuo.

If, however, the second phase has stronger interatomic bonds and a higher melting temperature than the basic solid solution, it may, conversely, increase the heat resistance of the alloy. According to A. A. Bochvar [444] heterogenization of the structure due to such phases may serve as an effective method of increasing the heat resistance of alloys employed as cast. It cannot be used in deformable alloys, since the phases split up and pass through processes of coagulation and spheroidization. It is highly important here, however, that

¹H. V. Pridantsev and G. V. Estulin. *Stal'* [Steel], No. 7, 1957, p. 636; cf. also [916].

the corresponding phases not be capable of solution in the basic mass. The heat resistance may otherwise not only fail to increase, but even decrease because a "solution" plasticity mechanism begins to play the dominant role. A predominance of the negative effect, caused by the "solution" mechanism of the process, over the positive effect of heterogenization was observed, for example, in a copper-based alloy [577].

The phases which increase the heat resistance may be formed in the grain boundary layers by the impurities contained in the alloy or by admixtures of certain elements introduced in insignificant quantities. Thus, for example, the addition to aluminum of iron even in the amount of 0.05% doubled its heat resistance (as determined by the long-term hardness method), while with an iron content up to tenths of one percent the heat resistance of the aluminum was tripled or quadrupled, apparently due to precipitation of the $FeAl_3$ on the grain boundaries and between the branches of the dendrites [837]. In certain steels a similar part is, apparently, played by the addition of insignificant quantities of boron, but still many times greater than the quantity of it introduced into structural steels to increase their hardenability. As is to be seen from Figure 314 [839], which pertains to austenitic steel with 15% Cr and 25% Ni, the total deformation decreases greatly upon introduction into it of up to 0.1-0.15% B and increases again only with increase in the latter.

Precisely this circumstance permits the assumption that the positive effect of boron on the heat resistance of steel comes as the result of the formation by it in the grain boundary layer of a new phase, and not as a result of its entering the solid solution. According to our theory (see [Russian] pp. 93 and 167), the boron, being in a solid solution, just as carbon, reduces the interatomic bond strength and consequently should not increase the heat resistance. V. I. Prosvirin and others [839] found, by the vacuum thermal method of microstructure investigation, that in the austenitic steel referred to, when it contains up to 0.12% B, a phase is detected along the grain

boundaries which they assume to be a solid solution of boron in austenite. We, on the other hand, are inclined to consider this phase as chromium boride. The high heat resistance of the latter favors such an assumption. In fact, as is to be seen from Figure 354 below, the heat resistance of chromium boride at 980° is only slightly less than the heat resistance of a chromium based alloy at 650° . Hence it is quite probable that it is the chromium boride which, being located in the boundary layer of the grain, causes increase in the heat resistance of a steel alloyed with boron.

The most important phases capable of increasing the heat resistance and thermal stability of alloys based on iron, nickel, and cobalt are metallic compounds and carbides. In this connection it is necessary to discuss in somewhat greater detail the part played by carbon. Being in the solid solution (in the austenite) and decreasing the strength of the interatomic bond,

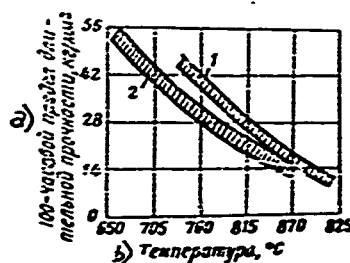


Figure 313. Effect of melting method on the heat resistance of nickel-based alloys (11 in Table 96); 1 - melting in vacuum; 2 - melting in open furnace; (a) 100-hour long-term ultimate strength, kg/mm²; (b) temperature, °C.

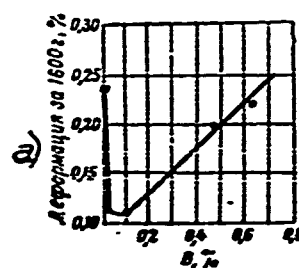


Figure 314. Effect of boron on deformation of specimens of Xh15W25 steel in 1600 hours at 700° and stress of $\sigma = 6 \text{ kg/mm}^2$; (a) deformation in 1600 hours, %.

carbon lowers the heat resistance in the event diffusion plasticity mechanisms predominate, but may raise it if slip mechanisms predominate. Thus, with a short service life, high stress, and moderate temperatures, even dissolved carbon (in austenite) will increase the heat resistance. At high and very

high temperatures, on the other hand, even the short-term strength will be lowered by dissolved carbon, as is observed in experiments [cf. 440].

If the carbon is bound in the carbides, it may increase the heat resistance also when diffusion plasticity mechanisms predominate. But the direction and extent of the effect of the carbon bound in the carbides depend not only on the length of service and the operating temperature, but also on the composition of the carbides, which determines their resistance, on the shape, degree of dispersion, and location of the carbides. Thus, for example, increase in carbon content from 0.13% to 0.45% increased the creep resistance of Kh14Kh14V2M austenitic steel at 500° and 600°, but only ~10% [852]. Only by making allowance for the entire array of factors, insofar as this is feasible at the present time, is it possible to give a more or less satisfactory explanation of the contradictory data encountered concerning the effect of carbon on the heat resistance and thermal stability of steel.

Figure 15 [822] illustrates the combined effect of carbon and nitrogen¹ (nitrogen exerts an effect in the same direction as carbon, but a fainter one) on the time to failure and creep rate of a steel of the Kh18N9 type at various temperatures and stresses. Prior to testing, the steels were quenched from 1120° in water. The decrease in the time to failure and the increase in the creep rate up to a certain carbon content at test temperatures of 650 and 700°, when diffusion plasticity mechanisms predominate, may be ascribed to the fact that a certain amount of carbon in the base in question is preserved in the solid solution (cf. Fig. 366), decreasing the interatomic bond strength. With a higher content, the carbon is precipitated from the solid solution in the form of dispersed carbides, increasing the heat resistance. Hence the extent of lowering of the heat resistance by the dissolved carbon is intensified with rise in temperature and with decrease in the stress, when there is

¹The nitrogen content increased from 0.005% in steel with 0.001% C to 0.05% in steels with 0.12 to 0.16% C.

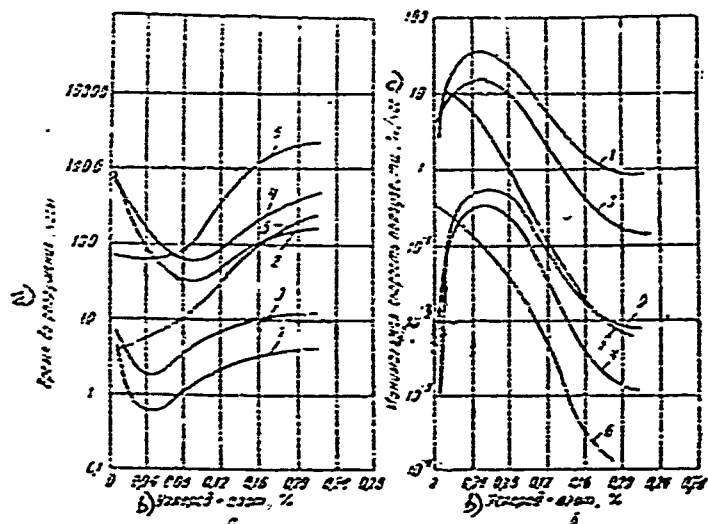


Figure 315. Combined effect of carbon and nitrogen on the time to failure (a) and creep rate (b) of austenitic steel of the Kh18N9 type at various temperatures and stresses:

- | | |
|-------------------------------------|-----------------------------------|
| 1 - 17.5 kg/mm ² at 700° | 4 - 14 kg/mm ² at 650° |
| 2 - 10.5 kg/mm ² at 700° | 5 - 35 kg/mm ² at 540° |
| 3 - 21 kg/mm ² at 650° | 6 - 28 kg/mm ² at 540° |

(a) time to failure, hours; (b) carbon + nitrogen, %; (c) minimum creep rate, %/hour.

a greater development of diffusion processes. At a lower stress the effectiveness of action of the carbides also weakens, and more carbon is required to increase the heat resistance. The great negative effect of the dissolved carbon, apparently, indicates that the grain boundary layers, which play a decisive part in this case, are highly enriched with carbon. At 540° slip plasticity mechanisms predominate, in consequence of which the carbon constantly increases the fire resistance; however, at a lower stress the dissolved carbon does not increase the time to failure even at this temperature, and even reduces it somewhat. It should be noted that the authors of [522], from which Figure 315 is taken, attempt to explain the minima in Figure 315a and the maxima in Figure 315b by the strengthening effect of a special form of

ferrite, the amount of which in hardened steel, according to their investigations, decreases from $\sim 35\%$ at $0.001\% \text{ C}$ to 0% at $\sim 0.1\% \text{ C}$, but such an explanation is highly dubious.

The effect of the composition of the carbides is apparently manifested chiefly in the circumstance that when complex, more stable carbides are present in the steel, the negative effect of the "solution" plasticity mechanism is exhibited to a far lesser extent at the operating temperatures, and their positive influence on the heat resistance is found to be more effective. Thus, for example, it is to be seen from Figure 316 [712] that for carbon steel heated under load in vacuo at 650° , with increase in the carbon content from 1.25 to 1.65%, and hence in the amount of carbides as well, the time to failure of the specimen decreases, while chromium carbides in steel of the Kh18N9 type greatly increase the time to failure. It is true that in the steel of the Kh18N9 type the carbides were dispersed and, apparently, situated along the grain boundaries. But there was no such difference in the carbon steels in Figure 316. Nor can one ascribe the lower fire resistance of the steel with 1.65% C to brittle failure due to lowered tear resistance as against the steel with 1.25%, since it failed at a much greater elongation than the latter.

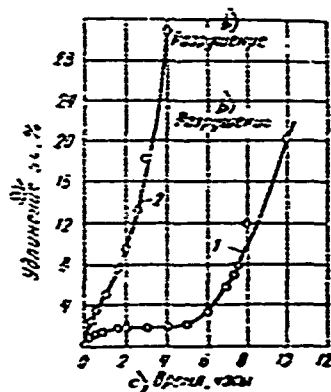


Figure 316. Deformation of specimens of carbon steel with 1.25% (1) and 1.65% C (2) heated in vacuo at 650° under a stress of $\sigma = 8.9 \text{ kg/cm}^2$.
(a) elongation, l, %;
(b) failure; (c) time, hours.

In thermally stable pearlitic and martensitic steels which contain no elements forming highly stable carbide phases, the resistance of the carbides

is apparently still not sufficient substantially to weaken the effect of the "solution" plasticity mechanism. Hence the increased carbon content of such steels may be utilized to raise the creep resistance only at temperatures up to $\sim 400^{\circ}$. The thermal stability is raised at higher temperatures with increase in the carbon content only in the event of a short service life, and drops in the event of prolonged action of a load. Unfavorable situation of the carbides along the grain boundaries may serve as an additional cause of decrease in the thermal stability of steel by carbon, this leading to pressure brittle intercrystalline failure. The latter was observed in experiments during the creep testing of steels with 4.5% Cr, 0.40% and 0.68% C first subjected to .enching and tempering at 650 to 700° [64].

Strengthening of thermally stable and heatproof steels

It follows from the foregoing that the basic method of obtaining heat-proof and thermally stable steels and alloys (based on other metals) consists in strengthening the solid solution through alloying, (depending on what the service conditions of the alloy are to be, either primarily of the boundary layers or of the grains themselves) and in creating heterogeneity owing to phases satisfying definite conditions. Subsequent strengthening of the alloy can be achieved basically through the conventional treatment methods: temper hardening (for steels of the pearlite and martensite class), precipitation hardening, or work hardening. However, the peculiarity -- and under certain service conditions of an alloy the very advisability -- of employing a given hardening treatment are due to the fact that at high temperatures, as has already been pointed out, the tendency of the alloy toward thermodynamic balance can be realized. It is advisable to harden alloys with a short service life which work under high load and at moderate temperatures by creating a more metastable structure in them. In alloys intended for lengthy service under small load or at high temperatures, on the other hand, it is necessary in

hardening to strive to ensure the maximum possible stability of the structure, including that of the solid solution itself. Thus, thermally stable pearlitic steels which have been normalized and subjected to quenching and tempering are equivalent as regards the short-time strength values. At 425° they are also practically equivalent with respect to creep resistance. However, at a higher temperature, quenched and tempered steels are far inferior to normalized steels with respect to creep resistance [cf. 640].

Carbides and metallic compounds are employed as the strengthening phases in strengthening through precipitation hardening, which is employed for the majority of the modern heatproof chrome-nickel austenitic steels and nickel-based alloys. It is highly important here, particularly for alloys intended for parts with a lengthy service life, that the strengthening phase possess high resistance to coagulation, which determines the softening of an alloy at the operating temperature. As was pointed out during the discussion of the general effect of alloying elements, and of methods of assuring the red-hardness of high-speed steel, the resistance of the carbide or metallic compound to coagulation is the greater, the higher is the interatomic bond strength in the lattice of the basic solid solution and of the strengthening phase itself. However, certain carbides have interatomic bonds of such high strength that they are not changed to solution upon quenching, even from very high temperatures. Their high resistance to coagulation can, of course, not be used. It is found advantageous in this case (see [Russian] p. 198) to introduce into the composition of the alloy, and accordingly that of the carbide, an additional element which lowers the interatomic bond strength, this making it possible to change the carbide in solution at still acceptable quenching temperatures, although the resistance of the carbide to coagulation is thereby lowered.

The intermetallic phases capable of causing the effect of precipitation hardening in iron-nickel alloys, nickel, and nickel-based alloys are formed,

as has long been established, upon the introduction into these alloys of a number of elements such as aluminum, titanium, niobium, zirconium, beryllium, tin, etc. Certain of them, titanium for example, are used for strengthening alloys of the Invar and Elinvar type by precipitation hardening. The Ni_3Ti , Fe_3Nb_2 phases, etc., are also used in heatproof alloys.

A highly effective phase and hence the one the most widely used at the present time is that formed upon simultaneous introduction of titanium and aluminum into alloys also alloyed with chromium (principally with the aim of increasing the fire resistance). This strengthening α' phase, which is precipitated upon decomposition of the solid solution of a nickel-chromium-titanium-aluminum alloy and which contains, in addition to nickel, 14% Ti, 2% Al, and 2% Cr, as has been established experimentally by G. V. Kurdymov and others [355], has very strong interatomic bonds. These investigators found a great interatomic bond strength in the lattice of the solid solution of nickel with 20.15% Cr, 2.48% Ti, 0.6% Al, and 1.9% Fe, this strength being due to the solution in it of titanium, aluminum, and chromium, the combined effect of which results in a greater increase in the interatomic bond strength than in the corresponding binary solid solutions. The α' phase consequently possesses a high resistance to coagulation, this imparting to the alloy a high stability toward softening. But certain elements may lower the resistance of this phase, and accordingly the heat resistance of the alloy, by virtue of the fact that they either extract from it a portion of the titanium (carbon forming TiC) or themselves become part of it (manganese)¹.

A certain quantity of the carbides is always present in austenitic steels, as well as in nickel and cobalt-based heatproof steels, even in the event of a low carbon content of the former. Hence in such alloys one must apparently always reckon with at least partial hardening owing to the carbide phase,

¹Cf. E. V. Pridantsev and G. V. Estulin. *Stal'*, No. 7, 1957, p. 636.

proceeding either simultaneously with the process of precipitation hardening due to the intermetallic phases or independently. However, if the carbides must serve as the basic strengthening phase, an increased amount of carbon (up to $\sim 0.4\%$) is introduced into the alloy. The composition of the carbides depends (cf. [Russian] p.60) on the atomic ratio of the carbide-forming element and the carbon. Since all heatproof alloys contain a large amount of chromium, the basic carbide in them is Cr_{23}C_6 , in which the atoms of other elements also are dissolved by substitution. Other alloying elements introduced into these alloys with the aim of hardening the solid solution or of forming a strengthening intermetallic phase are at the same time usually carbide-forming elements as well, for example, tungsten, niobium, molybdenum, titanium, etc. In this case carbides whose base is comprised by these elements are also discovered in the alloy. Finally, an important part is also played by the nitrogen contained in these alloys, which replaces a portion of the carbon atoms in the lattice of the carbides, which are thus carbonitride phases [cf. 785, 841, etc.].

All these phases possess a very strong interatomic bond, while the elements forming them reinforce considerably the interatomic bond in the solid solution. Hence they are converted to solution at very high temperatures and fall from solution also at high temperatures, over 500 to 600° , and in the 600 to 850° range in a number of alloys, and slowly coagulate. It is advisable to subject parts made of such alloys and intended for lasting service to anneal after quenching, at a temperature 100 to 120 or 150° higher than the operating temperature. On the other hand, it is better to subject parts with a short service life, particularly those in service at high temperatures, only to quenching, from a temperature at which the carbide phases are liable to dissolve. In this case the carbides will be precipitated from the solid solution directly at the operating temperature under a stress the action of which must intensify this process, and coagulation of the carbides does not have

time to occur. The creep resistance of the alloy will thus be higher.

It must be borne in mind, however, that more intensive precipitation of carbides in the event of service of the alloy under stress also leads to more intensive embrittlement of the grain boundaries, along which the carbides are primarily situated. Thus it is to be seen from Table 88 [449] for a steel with 0.51% C, 13.6% Cr, 14.47% Ni, 0.76% Mo, and 2.43% W, that after 100-hour heating at 800° under load the plasticity characteristics and the resistance to fracture at room temperature have lowered, while the resistance to plastic deformation has increased to a much greater extent than after the same heating but with no load.

Table 88

Mechanical Properties of El69 Steel at 20° Under Various Conditions

Condition of steel	$\sigma_{0.2}$ kg/mm ²	σ_b kg/mm ²	S_k kg/mm ²	$\delta, \%$	$\psi, \%$	Nature of Failure
Quenching from 1180° (initial condition)	37.2	79.2	170.1	46.2	60.7	Plastic, along grain
Heating ¹ , after quenching, at 800° for 100 hours and $\sigma = 6$ kg/mm ²	{ 45.0 - }	{ 91.0 92.0 }	{ 125.0 123.0 }	{ 20.0 18.2 }	{ 29.0 24.0 }	Brittle, along grain boundaries.
Heating ¹ , after quenching, at 800° for 100 hours, but with no stress	{ 40.0 42.6 }	{ 84.2 84.5 }	{ 137.0 131.0 }	{ 23.5 21.5 }	{ 47.0 43.0 }	

¹Two specimens treated.

Certain heatproof austenitic steels, most frequently those intended for the manufacture of turbine disks, are additionally strengthened by work hardening, which is usually imparted to the forged piece by the partly hot method, i. e., at an elevated temperature, but one located beneath the recrystallization temperature. The basic condition of retention of the strengthening effect

of the work hardening in the process of service lies in the circumstance that the operating temperature must be lower than the recrystallization temperature for the given steel. The duration of action of temperature also has an effect on softening a work-hardened metal. Thus, for example, in work-hardened copper heated at 280° for 500 hours hardness was still fully retained, and was removed after 1000 hours; at 320° the hardness was fully removed after as little as 100 hours [842]. Consequently, the longer the service life of the part, the greater must be the difference between the recrystallization temperature and the operating temperature.

The recrystallization temperature is much higher for gamma iron than it is for alpha iron. Alloying elements cause additional increase in the recrystallization temperature [cf. also 445], so that for austenitic steel, even with moderate degrees of reduction, it is 800 to 820° [cf. 783], and for certain high-alloy steels it is around 900° [cf. 41]. The recrystallization rate in austenitic steels is also low. Thus, favorable conditions are present for austenitic steels from the standpoint of thermal softening for the use of work hardening as a method of increasing the fire resistance, particularly with relatively slight degrees of reduction, of the order of 10%. It is reported [752] that for a steel with 16% Cr, 13% Ni, 2% Mo, 1% Nb, and 0.15% N from which a steam-turbine disk was manufactured, the hardening effect of semi-hardening with a subsequent 10% reduction was still fully retained after testing at 600° under stress for 30,000 hours. Extrapolation to 100,000 hours yields for this steel in the hardened state without cold working a long-term ultimate strength value of 9 kg/mm^2 , and 15 kg/mm^2 for work-hardened steel. Thread cutting has a substantial effect for austenitic bolts at operating temperatures up to 650° [752].

However, the possibilities of using the hardening effect of cold working are limited not only by the thermal softening of the material, but also by the fact that cold work, in intensifying the diffusion mobility of the atoms at

high temperatures, apparently accelerates the process of failure with time and the processes resulting in embrittlement of the grain boundaries in steels in which these processes may occur. Thus, in investigations by S. T. Kishkin and others [cf. 622, 760], with a nickel-based alloy with 20% Cr, 2.5% Ti, and 0.75% Al, under the effect of preliminary work hardening by 10% extension over the 100-hour long-term ultimate strength at 700° dropped from 42 to 22 kg/mm², despite the fact that the recrystallization temperature of this alloy is over 800°. If the hypothesis concerning such an effect of cold-working is correct, then there must also exist a certain optimum degree of work hardening for a given material, given operating temperature, and period of service, up to which the long-term strength will rise as against the state not affected by cold working, and then will begin to drop. Data are to be found in the literature, for example for work-hardened copper [642], which actually permit the inference of such a tendency. The positive effect of cold working may also be replaced by a negative one in the event of application of too high a working stress.

Mention should be made in conclusion of the effect of the grain size on heat resistance. It follows from what has been stated about the role of the boundary layer of the grains in processes determining the heat resistance characteristics, that under conditions in which diffusion plasticity mechanisms predominate a coarse grain must have a positive effect on the heat resistance of metals and alloys. This is confirmed by numerous observations and experiments. Thus, for example, it was noted very long ago [629] that a fine-grained tungsten wire in electric incandescent lamps flows at the operating temperature and fails under the influence of its own weight much more rapidly than does a coarse-grained one. A substantial increase in the creep limit of austenitic steel with coarsening of its grain has also been observed [436].

In solving the problems of the optimum grain size, it is necessary also to reckon with the effect of this factor in other directions, as well as with

its indirect effect through other processes, which may be both positive and negative. Thus, for example, coarsening of the grain leads simultaneously to a sharp drop in plasticity in the hot condition, although the plasticity increases at room temperature.

B. THE ROLE OF ALLOYING AND OTHER FACTORS IN INCREASING THE CORROSION RESISTANCE (SCALE RESISTANCE) OF STEEL

General principles

The term corrosion resistance is understood to mean the resistance of a metal or alloy to the action of various gaseous media (gas corrosion) at high temperatures. A particular case, but the one the most frequently encountered in practice and hence the most important one, is the process of oxidation at high temperatures. The resistance of steel to gas corrosion is affected by a number of factors, the most important of which are the composition of the medium, the temperature and periodicity of its change, the duration of the holding period, the gas flow rate, the condition of the surface of the metal or alloy, and the composition of the latter.

The relative position of metals with respect to their resistance may change in different media and at different temperatures. Certain metals and alloys corrode rapidly and fail in specific media in consequence of the formation of certain compounds, which in turn may either exert a direct harmful effect or lower the resistance of the alloy by changing its composition. Thus, for example, in alloys alloyed with chromium, when heated in a carburizing medium, carbides are formed, and nitrides upon heating in a medium of nitrogen. A portion of the chromium is hereupon bound and the basic mass of the alloy is impoverished with respect to chromium. Sulphur dioxide at certain temperatures has the greatest effect on nickel, a lesser effect on cobalt, iron, and tungsten, and a very slight effect on chromium and copper. The low resistance of nickel is explained by the fact that the Ni_3S_2 compound forms with nickel a eutectic which has a melting point of 645° .

Hydrogen sulfide has a greater effect than sulphur dioxide. As has been shown in a number of studies, alloys of iron with chromium and nickel in sulphur dioxide become unstable at temperatures above 400° , and in hydrogen sulfide even at temperatures above 300° . This is explained by the fact that in the first case the presence of oxygen leads to the formation of an oxide film which protects the surface of the metal from interaction with sulphur. This hypothesis is confirmed by production studies [775] in which it was found that heating of chrome-nickel austenitic steels in an oxidizing medium protects them better from the action of the sulphur dioxide contained in the gases.

Hence the use of alloys alloyed with nickel at high temperatures in media containing sulphur compounds is not to be recommended. However, with the medium containing up to 0.1% S, chrome-nickel alloys have a resistance which is still sufficiently high [776]. The introduction of silicon into chrome-nickel steel increases the resistance of the latter in a sulphurous medium [776]. Contrary to expectations, nickel-based alloys of the Nichrome type are found to be fairly resistant to sulphur compounds, both in an oxidizing and in a reducing medium [775 et al.].

Studies made in recent years of the corrosion of steels and alloys in the synthetic combustion products of fuel of various types and grades with reference to gas turbines have shown [776] that vanadium contained in fuel has a great adverse effect. Being converted in the form of vanadium pentoxide into ash which is carried along by the flow of gases, it contributes to the corrosion failure of heatproof alloys, particularly those alloyed with molybdenum, of which gas turbine parts, including the vanes, are made. Increase in the amount of sodium sulfate in the ash containing V_2O_5 at temperatures above 850° reduces its harmful effect. The mechanism of the effect produced by vanadium pentoxide has not yet been established. In particular, an hypothesis is advanced to the effect that vanadium compounds, which have a low melting point, contribute when in the liquid phase to breakdown of the protective film forming on the steel or alloy. This may be the reason for the harmful effect of

vanadium, which is contained in the alloy itself, on the latter's corrosion resistance. At any rate, one of the methods of diminishing the corrosive action of a medium containing a vanadium compound is introduction into the fuel of substances which elevate the melting point of the ash, particularly calcium and nickel compounds.

If there are no sulphur or other harmful compounds present in the fuel combustion products, the oxidation rate increases with increase in their content of free oxygen. The oxidation of steel occurs in dry oxygen at a rate several times more rapid than oxidation in dry air, and usually more rapidly in a medium of carbon dioxide than in air and oxygen. Oxidation proceeds at an even faster rate in water vapor.

Increase in the gas flow rate intensifies the oxidation only up to a definite value of the latter. The flow rate subsequently ceases to have an effect, probably because increase in the amount of gas coming in contact with the heated metal is offset by decrease in the period of this contact.

The oxidation rate of metals and alloys and the effect of temperature on it are determined by the fact that this is a diffusion process. Moreover, the possibility of occurrence of two-way diffusion have been demonstrated: that of atoms, or, as some assume, of ions of the metal through the layer of scale toward the outer surface of the article, and counter-diffusion of oxygen atoms or ions toward the metal-oxide interface. Diffusion of the atoms of the metal through the scale predominates in the case of oxidation of iron and its alloys. Oxygen diffusion [452] plays the dominant role in the oxidation of nickel and chromium.

Numerous studies, particularly those of V. I. Arkharov and his associates [452, 450] show that the diffusion permeability and, accordingly, the protective properties of the scale are determined by the crystallographic type of its lattice, and for identical types of lattice, by the crystallographic characteristics of the latter: its spacing, number of vacancies, etc.

Moreover, the interatomic bond forces in the lattice of the oxide phase must play a prominent part, as they do in metal alloys: increase in the bond forces leads to retardation of the diffusion processes. All these factors may change both under the effect of the oxidation conditions and as a result of alloying.

The composition and type of the scale lattice are determined basically by the metal-oxygen phase diagram and also depend on the composition of the medium, since the chemical conditions of oxide formation may vary for different media. Thus, the scale which forms on iron when the latter is heated in air, oxygen, and in mixtures of oxygen or air with water vapor, consists of three layers: an inner one of wustite FeO , a center one of magnetite Fe_3O_4 , and an outer one of hematite Fe_2O_3 [450]. Upon heating in water vapor or carbon dioxide, on the other hand, the scale on the iron consists of only two layers, wustite and magnetite. Hematite is not formed in this case, since the dissociation pressure of this oxide is greater than the partial pressure of the oxygen formed as a result of dissociation of the water vapors or carbon dioxide [733, p. 52]. The scale on nickel, according to the data of most studies, consists of the oxide NiO alone. There is no doubt about this, at any rate, at temperatures above 1100° .

The oxidation rate in the initial stage, when the thickness of the scale is still very slight, is determined by the rate at which the chemical reaction itself proceeds. After a certain period, when the process has become steady, its rate is determined by diffusion of the metal or oxygen through the layer of scale. In this stage, which is the most important one for practical purposes, the process of growth of the entire scale and its individual layers conforms (occasionally with slight deviations) to a parabolic curve, i. e., is greatly retarded in the course of time. As an example, Figure 317 (V. I. Tikhonirov et al. [733]) shows the rectilinear dependence of thickness squared on time for each layer of a scale on iron heated in air at 600° . It also follows that the proportion of the thicknesses of the individual layers of the

scale remains constant throughout the oxidation period at the temperature in question.

The effect of the temperature consists not only in a general increase in the oxidation rate in conformity with increase in the rate of diffusion of the metal or oxygen, but also in modification of the composition and structure of the scale and the proportion of the thicknesses of its individual layers. It is to be seen from the diagram in Figure 318 (V. I. Tikhomirov et al. [753]) for iron which has been subjected to oxidation in air, that no wustite is formed below 575° , since the latter is thermodynamically unstable at these temperatures. The amount of wustite grows sharply above 575° due to decrease in the amount of magnetite and hematite, and above 700 to 750° the thickness of the wustite layer comprises 94 to 95% of the thickness of the entire scale. This agrees satisfactorily with the iron-oxygen phase diagram. In conformity with the latter, a second phase, secondary magnetite, is detected in wustite observed after cooling of the specimen. It was also established radiographically in a number of projects by V. I. Arkharov et al. [452] that in the outer layer of the scale there arises a texture $(11\bar{2}) \alpha\text{-Fe}_2\text{O}_3 \parallel (110) \text{Fe}_3\text{O}_4 \parallel$ to the outer surface in the "intermediate" temperature range of 600 to 800° . Above 900 to 1000° , this texture is replaced by the "high-temperature" texture $(111) \alpha\text{-Fe}_2\text{O}_3 \parallel (100) \text{Fe}_3\text{O}_4 \parallel$ to the outer surface. The texture reorientation temperature rises with increased holding time. According to their data, the hematite in the surface zone of the scale contains, in the initial stage of oxidation, an excess number of oxygen atoms implanted in the interstices (α''), as against stoichiometric Fe_2O_3 . During the subsequent stages of oxidation its lattice changes into one with vacant points, the vacancies remaining at the sites of the iron ions (hematite α''').

This also determines the kinetics of oxidation of iron at various temperatures and lengths of the test period, as shown in Figure 319 [452]. With

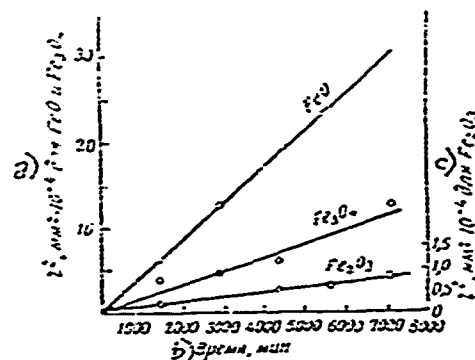
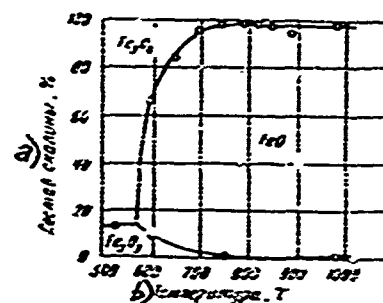


Figure 317. Growth of individual layers of scale on iron at 600° in ambient air.

(a) $l^2 = 10^{-4}$ for FeO and Fe₂O₃; (b) Time, minutes; (c) $l^2 = 10^{-4}$ for Fe₃O₄.

the appearance of the wustite phase, which is a substitutional solid solution with a deficiency of iron atoms (see page 63), from being faint (below 500 to 550°) the oxidation becomes moderate in the "intermediate" stage (600 to 800°), and then intense (above 900 to 1000°), the latter condition being due to the free-point lattice of the hematite α''' . The temperature at which trend of the kinetic curve changes (Fig. 319) is the higher, the shorter is the holding time. No free points were detected in the lattice of the NiO oxide. Hence, the diffusion of nickel atoms through the oxide layer is impeded. And since diffusion of oxygen atoms through this layer proceeds slowly, oxidation of nickel is more difficult than that of iron.

Figure 318. Change in composition of scale on iron versus heating temperature in ambient air. (a) scale composition, %; (b) temperature, °C.



Periodic abrupt temperature changes accelerate the oxidation process. This is probably to be ascribed to the stresses arising in the layer of scale and facilitating local failure of the layer. This circumstance is of the

greatest importance for high resistance alloys from which heating elements are manufactured.

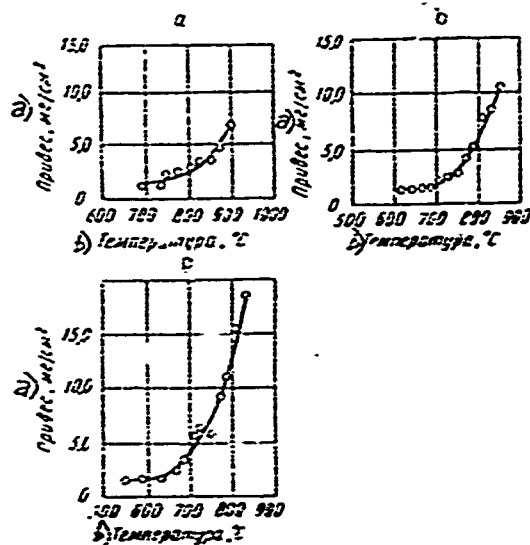


Figure 319. Increase in weight of arasco iron specimens versus temperature for various holding periods:

a - 20 min; b - 2 hours; c - 12 hours;

(a) weight increase, mg/cm^2 ; (b) temperature, $^{\circ}\text{C}$.

Effect of alloying elements and impurities

The role of alloying elements consists primarily in their modifying the composition and structure of the scale and the interatomic bond forces in it, and consequently also the kinetics of the process of steel or alloy oxidation. Thus, for example, according to studies by V. V. Ipat'yev et al. [733, p. 68], an induction period is observed when chromium steel is oxidized in air, i. e., for a certain period the oxidation rate is very low and proceeds parabolically with time only after this period. As may be seen from Figure 320, based on their data for a steel with 0.15% C and 12.65% Cr, the length of the incubation period decreases with elevation of the heating temperature. The same is observed upon increase in the oxygen content in the gaseous mixture. With a

steel with 0.5% C and 5.82% Cr, an incubation period upon oxidation in air was observed [733, p. 126] only at 100 and 800°. Chemical, microscopic, and radiographic investigations of scale have shown that a film of the oxide Fe_2O_3 , highly enriched with chromium as against its content in steel (55.5% Cr versus 12.98% Cr in steel), is formed on the surface of the steel in the course of the induction period. Diffusion proceeds at a very low rate through this film, in consequence of which oxidation practically comes to a halt by the end of the induction period. Spinel, FeCr_2O_4 , which has a higher permeability than the Fe_2O_3 phase, is subsequently formed. The increase in the amount of the Fe_2O_3 phase occasioned by the decline of the Fe_2O_3 phase, as well as the simultaneous increase in the amount of Fe_2O_3 in the outer layer through diffusion of the iron, leads to increase in the permeability of the scale. This corresponds to the second stage of the process, when the oxidation rate conforms to the parabolic law.

The same studies (with steel with ~6% Cr) demonstrated that the outer part of the scale on chromium steel; as on iron, consists of three layers: an outer one I, hematite; II, magnetite; and III, wustite. The wustite layer is followed by an inner layer, IV, adjoining the metal which consists of chrome spinel $\text{Fe}_3\text{O}_4 \cdot \text{Cr}_2\text{O}_3$ and wustite. The chromium is concentrated only in this inner layer of the scale and is absent from its outer "iron" layers. This is explained by the very low rate of diffusion of chromium through the scale as compared with iron diffusion. It is consequently assumed that the outer layers of the scale are formed chiefly through diffusion of the iron through it, while the inner layer, which contains all the chromium, is formed through counter diffusion of the oxygen from the gaseous medium. In the stage when the process follows a parabolic curve, the interrelation of the thicknesses of the individual layers of the scale, as on iron, remains constant with respect to time, but varies with change in temperature. An effect is exerted here by alloying elements, in this instance chromium, on the iron-oxygen phase

diagram. Thus, an appreciable amount of rustite appears on chrome steel not after 575°, as on iron, but only after 900°. The thickness of the rustite layer here is also many times smaller than under the same conditions in iron.

Thus the presence of an inner difficultly penetrable layer of chrome spinel, the slight thickness of the rustite layer, and the location of the latter between the spinel layer and the hematite, rather than between the metal and the hematite, are actually conducive to the much higher corrosion resistance of chrome steel as compared to iron and carbon steel. Moreover, as has recently been demonstrated [452], the presence of chromium in the oxide phase increases the interatomic bond forces in the latter.¹

It is to be seen from Table 69 [451] that not only chromium, but many other alloying elements as well, are concentrated in the inner layer of scale adjoining the metal, this apparently being attributable to the low rate of their diffusion as compared with the iron atoms (the presence of a certain quantity of the alloying elements in the outer layers, according to the hypothesis of V. V. Ipat'yev and others, is explained by inaccurate separation of the scale layers in study of their composition). However, far from every alloying element is capable of increasing the corrosion resistance of steel. For this purpose it must still meet the following basic requirements.

The oxide film formed by the element must be strong and dense. It is necessary for this purpose, as we know, that the molecular volume of the oxide be greater than the atomic volume of the metal for which it was formed, this amounting to the inequality

$$\frac{mD}{m_d} > 1.$$

¹It is true that this was established with synthetic hematite, while the hematite layer on chrome steel contains no chromium. It may be assumed, however, that the chromium increases the interatomic bond forces in the lattice of the spinel phase as well.

where w is the molecular weight of the oxide;

F is the atomic weight of the metal;

a is the density of the film;

D is the density of the metal.

Table 89

Enrichment of Inner Scale Layer by Alloying Elements

Element	Steel	Content in steel before oxidation, %	Duration of holding in air at 1050°, days	Content, %, in scale layers ¹		
				1	2	3
Ni	Nick	2.75	6	0	0.16	7.97
Ni		36.0	15	1.46	2.29	52.95
Cr	Chrome	12.25	6	0.61	1.12	25.32
Ni	Chrome-nickel	5.18	6	0.48	0.64	8.57
Cr		0.85	6	0.14	0.16	1.83
W	Tungsten	5.5	6	0.67	5.55	9.67
V	Vanadium	0.27	7	0.08	0.16	0.40
Mn	Manganese	5.07	4	1.55	2.58	2.50
Mn		5.76	4	0.28	0.57	0.95
Si	Silicon	2.02	4	Traces	Traces	4.36

¹The nickel is in the scale in the metallic state; the remaining elements are present in the form of oxides.

The densest film is formed on iron or steel by chromium, the oxides of which have a density and molecular weight near those of iron oxides. Chromium is followed by aluminum and silicon.

The second requirement consists in the circumstance that the free energy of formation of the alloying element oxide must be greater than the free energy of formation of iron oxides. In this case the film will consist predominantly or entirely of the oxide of the element in question. A large number of elements, including chromium, aluminum, and silicon, meet this requirement.

Thus, chromium, aluminum, and silicon are the best suited as alloying elements which increase the corrosion resistance of steel. In fact, as may

be seen from Figure 321 [455]. For example, chromium and aluminum in binary alloys with iron sharply reduce the additional weight caused by their oxidation, the concentration of each of the elements needed to achieve this goal being the greater, the higher is the heating temperature of the alloy. Since the film is enriched by one of these elements at the expense of the iron, in the process of lasting service at high temperatures the content of the alloying element in the alloy decreases. A difference in concentrations between the core and surface is hereupon created: the content of the element is smaller in the outer layer of the alloy than in the center. Thus, in a binary iron alloy with 15% Al after heating at 1350° for 50 hours, a 0.76% decrease in the aluminum content in the outer layer of a specimen 20 mm in diameter as compared to its center (14.51% and 13.75%) [455]. A similar effect is observed with ternary alloys of iron with chromium and aluminum.

Of all the requirements referred to above which an alloying element must meet in order to increase the fire resistance of steel, its effect on the composition, structure, and properties of the scale is apparently the decisive one. Many elements for which the condition of formation of a dense oxide film is met do not increase the corrosion resistance of steel, and certain of them even lower it. Such elements, for example, are vanadium, molybdenum, tungsten, and boron. This is explained by the specific properties of their oxides. The volatile oxides of molybdenum not only disrupt the continuity of the film which forms on the steel alloyed by them but, coming in contact with the surface of other corrosion-resistant steels, in joint heating, for instance, also destroy the oxide film of the latter. The oxide films on steels alloyed with vanadium are easily fusible. The oxide of vanadium apparently dissolves the oxides of other metals, this contributing to lowering of the corrosion resistance.

Such an alloying element as nickel, on the other hand, increases the corrosion resistance of steel, at any rate in the case of oxidation in a

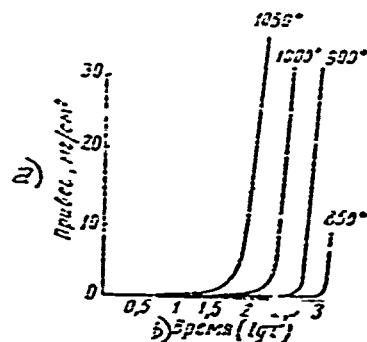


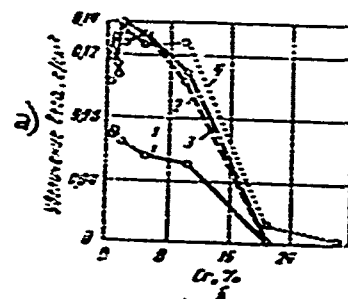
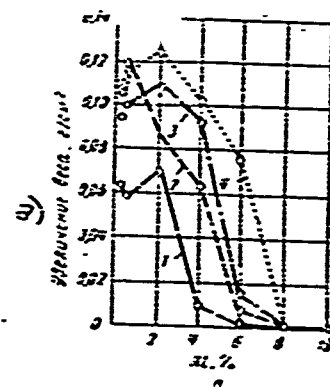
Figure 320. Duration of incubation (induction) period for 1Kh13 steel versus temperature. Air not dried.
(a) weight increase, mg/cm^2 ;
(b) time ($\lg \tau$).

medium of air. As may be seen from Figure 322 (based on research by V. V. Ipat'yev et al. [755, p. 80], in which the values of the oxidation rate constant at 940 are plotted against the composition for binary iron-nickel alloys, the greatest increase in the corrosion resistance of the latter occurs when the nickel content is raised to 20 to 25%. A study of the scale on these alloys has shown that the thickness of the wustite layer decreases upon the addition of nickel, and this layer is absent altogether from the scale when the alloy contains 25% Ni.

Figure 321. Effect of aluminum (a) and chromium (b) on the corrosion resistance of iron alloys at various temperatures:

1 - 15 hours at 900°; 2 - 75 hours at 1000°; 3 - 5 hours at 1100°; 4 - 2 hours at 1200°;

(a) weight increase, g/cm^2 .



Nickel additionally increases the corrosion resistance of steel alloyed with chromium, including austenitic steels. The extent of the effect of nickel on the corrosion resistance increases with elevation of the temperature.

Table 90.

Minimum Amounts of Nickel Required to Ensure Satisfactory
Corrosion Resistance* at Various Temperatures

Chromium Content, %	Minimum amount of nickel, %, at temperatures, °C, of			
	870	930	1070	1200
11	26	30	42	56
15	0	16	30	41
21	0	9	4	9**
26	0	9	3	5***
31	0	0	0	8

* An extent of corrosion not exceeding 2.5 mm/year has been adopted as the criterion of satisfactory corrosion resistance.

** The corrosion resistance is lowered somewhat with 20 to 50% Ni.

*** The corrosion resistance is lowered somewhat with 20 to 40% Ni.

As is to be seen from Table 90 [54], which pertains to industrial steels containing 0.55 to 0.40% C, up to 1.2% Si, and 0.8% Mn, when the steel contains more than 20% Cr, the minimum amount of nickel needed to assure satisfactory corrosion resistance even at 1200° does not exceed 8 to 9%. Of great interest is the fact that when the alloy contains over 50% Ni, i. e., in nickel-based alloys, even less than 12% Cr is sufficient, and when it contains over 60% even as little as 10% Cr, to ensure satisfactory corrosion resistance at 1200°. This fact, on which the corrosion resistance of Nichromes, alloys of the Nimonic type, etc., is based, is ascribed to the formation on the surface of the alloy of an oxide film consisting of spinel $\text{NiO} \cdot \text{Cr}_2\text{O}_3$.

Note should also be made of the circumstance, unfavorable for practical applications, that manganese oxides possess poor protective properties on both austenitic and ferritic steel. It is consequently far from always possible to substitute chromium-manganese steels for chromium-nickel ones as heat-resistant steels, despite the fact that chromium-manganese austenite is even superior to chromium-nickel austenite with respect to corrosion resistance.

The ordinary impurities have a negative effect on the corrosion resistance of metals. Thus, for example, commercial nickel oxidizes much more rapidly than does pure nickel. Annealing of nickel in vacuo, which results in additional removal of the impurities from it, appreciably reduces its oxidation rate [111]. Carbon and oxygen are particularly harmful in steels. The extent of their effect is not altogether uniform in different steels, this depending chiefly on the form in which they are present in the latter. In particular, carbon scarcely impairs the corrosion resistance of steel if it is dissolved in the basic mass of ferrite or austenite. By being present in steel in the carbides, on the other hand, carbon lowers the corrosion resistance of steel for two basic reasons: (1) due to the fact that it binds a greater or lesser amount of the basic alloying element, generally chromium, making the basic mass poor in the latter, and (2) due to the fact that the presence of a carbide phase renders the structure of the steel inhomogeneous. Intensification of the inhomogeneity of the structure is apparently also the chief cause of the harmful effect of the oxygen, since impoverishment of the basic mass in certain alloying elements (aluminum, silicon, chromium, etc.) bound with the oxygen can scarcely play a vital part, due to the insignificant quantity of the bound element. The inhomogeneity of the structure of the steel is intensified, on the other hand, when the oxides of such elements as have practically no effect on the corrosion resistance of the steel are present in it.

The effect of the carbon due to the first cause must naturally be the lesser, the more there is of the active alloying element in the steel. Never-

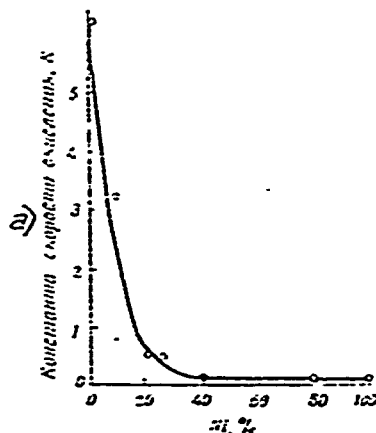
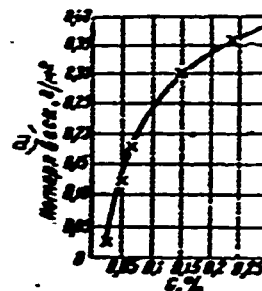


Figure 322. Effect of nickel on the corrosion resistance of Fe-Ni alloys at 940° in a medium of air.
(a) oxidation rate constant, \bar{K} .

theless, the negative effect of the carbon is considerable even in this case, as is to be seen, for example, from Figure 323 [453] for an alloy with 25% Cr and 5% Al, which was subjected to oxidation at 1200° for 240 hours. The weight losses corresponding according to this diagram to a definite carbon content are due, of course, to the total effect of the carbon. Hence the introduction into steel of a more energetic carbide-forming element than chromium, say titanium, reduces the harmful effect of the carbon but cannot eliminate this effect entirely, since the role of the carbides persists as a factor increasing the inhomogeneity of the structure of the alloy.

Figure 323. Effect of carbon on the corrosion-resistance of an iron alloy with 25% Cr and 5% Al. Heating at 1200° for 24 hours.
(a) Weight loss, g/cm^2 .



The corrosion resistance of steel apparently depends little on whether it is ferritic or austenitic at the operating temperature. Consequently, the effect referred to above of alloying elements and impurities applies basically both to ferritic and to austenitic steel. In particular, the effect of carbon becomes negative in austenitic steel as well when it is contained in an

amount such that a substantial quantity of chromium carbides which have not been converted to solution are present in the structure of the steel at the operating temperature.

We shall not deal here with the positive effect of very small additions of certain rare elements on corrosion resistance, since this effect is apparently due chiefly to the specific conditions of service of the heating elements.

Use has begun in recent years of metanics or cermetes as heat-resistant materials for a number of parts. Hence it is interesting to note that the mechanism of oxidation of such materials at high temperatures and the conditions which determine their corrosion resistance are fundamentally the same as for steels and alloys. Their oxidation rate as well is determined by diffusion of the ions of the metal and oxygen and of the carbon atoms through an oxide film, in consequence of which the composition and structure of the film plays a decisive part.

Thus, with a cermet based on titanium carbides and containing 20% Co [cf. 755], the oxide film formed upon oxidation in the 600 to 1000° temperature range consists of two layers; the outer layer consists of Co_3O_4 , or CoO , depending on the temperature, while the inner layer consists of rutile (TiO_2) with inclusions of metallic cobalt. The compounds CoTiO_2 and Co_2TiO_4 are also formed at 1100° as the result of reactions between the two layers. Upon addition of tungsten carbide in a quantity such that the oxide formed, W_2O_7 , is completely dissolved in rutile, the diffusion rate of the ions, and accordingly the oxidation rate, are reduced. If the quantity of the W_2O_7 formed exceeds the limits of its solubility in rutile, then CaTiO_3 , Co_2TiO_4 , and CoWO_4 appear in the oxide film in addition to the CoO and TiO_2 . This impedes diffusion, apparently, because of increase in the number of phase boundaries, and additionally increases the corrosion resistance. With an even greater quantity of the tungsten carbide, when the oxide film contains free W_2O_7 , the corrosion resist-

ance is impaired. The corrosion resistance initially drops upon the addition of the chromium carbide Cr_3C_2 . Only with such a quantity of the added chromium carbide that the quantity of the chromium oxide forming in the scale exceeds its limit of solubility in rutile is the fire resistance increased due to the CoTiO_3 and Cr_2O_3 . Upon the addition of tantalum and niobium carbides in the amount of 1%, the layer of scale after heating at 1000° for 75 hours consists of CoO , metallic cobalt, and a solid solution $(\text{Ti, Ta, Nb, Co})\text{O}_2$ of the rutile type. With a content of the tantalum and niobium carbides of 5 to 10%, the scale consists of CoO and $(\text{Ti, Ta, Nb, Co})\text{O}_2$, and with an even greater content only of $(\text{Ti, Ta, Nb, Co})\text{O}_2$.

3. THE PRINCIPAL TYPES OF THERMALLY STABLE AND HEAT RESISTANT STEELS AND ALLOYS AND THEIR MOST IMPORTANT CHARACTERISTICS

The variety of the requirements set for thermally stable and heatproof materials has led to the development of steels and alloys of various types which correspond to more or less concrete service conditions of articles, chiefly to a definite range of service temperatures, duration of load application, and magnitude of the latter. Pearlitic and ferritic-martensitic steels are employed as thermally stable steels up to a temperature of around 550°. As heatproof materials, i. e., at service temperatures above 550°, use is made, depending on the service conditions, either of austenitic steels or of nickel and cobalt-based alloys. Alloys based on chromium, molybdenum, and other high-melting metals have been developed in part, and are undergoing intensive development, for the highest service temperatures. Finally, for a number of machine parts use is made to a certain extent of special materials, also undergoing development, which consist of mixtures of various chemical compounds and metals and which are manufactured by the method of compacting and sintering; they are thus termed metamics or ceramets.

A. PEARLITIC AND FERRITIC-MARTENSITIC THERMALLY STABLE STEELS

Pearlitic steels

Pearlitic steels are less heatproof than the austenitic ones, but differ favorably from the latter in their lower thermal expansion coefficient, higher thermal conductivity, better technological properties (particularly, better hot deformability and machinability by cutting), higher notch-impact value, the possibility of modification of their properties over a wide range by heat treatment and the use of magnetic control methods, and their lower cost.

Lasting service at temperatures up to 550° may cause the following highly important processes in pearlitic steels: spheroidizing, coagulation, and change in the composition of the carbides, and hence in that of the solid

solution as well, graphitizing, processes imparting thermal brittleness to the steel.

The development of processes of spheroidizing and coagulation of the carbides is enhanced not only by long exposure of the steel to service temperature, but also by the service stress. The effect of the stress, which is confirmed in laboratory tests [845], is explained by acceleration of the diffusion. For the same reason preliminary cold working greatly facilitates globular formation and coagulation of carbides [443]. These processes lead to softening of the steel, both the short-term strength characteristics at room and elevated temperatures and the creep resistance being lowered. The report that the hardness of E1579 steel (Table 91), from which thick-walled pipes for hydrogenation plants had been manufactured, dropped from 280 to 160 H_B after service for 40 to 50 thousand hours at 550° and a pressure of 300 to 700 atm gives an idea of the possible extent of such softening. With specimens of this steel water-quenched from 1100°, the ultimate strength at room temperature dropped from 140 to 100 kg/mm² after tempering at 550° for 3000 hours [846]. The plasticity and impact ductility are hereupon generally increased to a greater or lesser extent.

The process of spheroidizing and coagulation of the carbides during service of a part can be greatly reduced by short-term holding of the part at a temperature 100 to 120° higher than the service temperature. This is the goal of stabilizing treatment of thermally stable steel. Data are given in the literature from which it is to be inferred that heating of steel at 650° for 5 hours renders it stable against spheroidization at 450° for 100 thousand hours, and that holding of around 10 hours at 650° is equivalent to 100 thousand hours at a service temperature of 500°. However, these data fail to allow for the accelerating effect of the service stresses. The carbide-forming alloying elements introduced into steel with the aim of raising its thermal stability also retard the processes of spheroidizing and coagulation by increas-

ing the interatomic bond strength in the carbide phase and the solid solution.

Less study has thus far been devoted to the changes in the properties of steel which are due to redistribution of the alloying elements between the solid solution and the carbide phase during the service of the part, i.e., as is generally the case, thermodynamic balance was not achieved upon preliminary tempering. It has been shown by experiment that the reduction of, say, molybdenum in the solid solution in the event of service for tens of thousands of hours at 540 to 550° may be substantial [916]. Hence much study is being devoted at present to the kinetics of these processes.

Effort to achieve full thermodynamic balance in a steel may lead to the process of graphitization during protracted service of the steel at elevated temperatures. Graphitization is observed the most frequently in the welded joints of high-pressure steam conducting pipes. The appearance of graphite, which has a low strength and is crystallochemically bound only weakly to the matrix, may lead both to softening of the steel and to premature brittle failure. At one time, certain investigators considered graphitization to be one of the causes of discontinuity of the straight line on the logarithmic stress-time to failure diagram (Figure 302c).

Study of this effect [617 et al.] has shown that the probability and extent of graphitization are influenced by the method of deoxidation of the steel, its composition and heat treatment, as well as by the stresses and work hardening. The two last-named factors contribute to graphitization apparently because they accelerate achievement of a state which is intermediate with respect to equilibrium, i. e., coagulation of the carbides, since coarse carbides are less resistant to graphitization than fine ones. Thus, for example, it has been demonstrated [847] that in the event of considerable creep the graphite formed does not have a round shape but less favorable elongated and radial ones. Apparently also related to the accelerating effect of stresses is the circumstance that graphitization proceeds more readily in welded joints. Hence

one of the methods of greatly reducing the tendency toward graphitization in the welded joint zone is high-temperature annealing of this zone, and an even better method is prolonged heating of the zone at a temperature somewhat higher than the A_{c1} point for the purpose of relieving the stresses.

Steel which has been deoxidized by aluminum in the amount of 0.02% or only by silicon is relatively resistant to graphitization. However, the introduction of 0.06% Al sharply increases the tendency of the steel toward graphitization. Attempts have been made to connect this circumstance to abnormality of the steel, i. e., to an increased rate of spheroidization and coagulation of the carbides. Within the limits of their usual content in steel, silicon and manganese have a slight effect on graphitization. As is to be expected, carbon favors graphitization. Hence it is recommended that the amount of carbon be kept at the lower limit in order to reduce the danger of graphitization.

Carbon steel possesses the greatest tendency toward graphitization. Of the alloying elements, molybdenum has an appreciable retarding effect. Thus, in steam pipes of carbon steel graphitization is usually observed at service temperatures above 425° , and in those of steel containing 0.5% Mo, above 480° . The positive effect of chromium is much greater; when present in an amount as little as 0.25% it compensates for the harmful effect of an increased amount of aluminum on graphitization. A simultaneous content in the steel of about 0.5% Mo and 0.5% Cr effectively prevents graphitization under the conditions possible in practice which have been studied thus far.

As a result of long service at elevated temperatures, thermally stable pearlitic steels may acquire a brittleness which according to A. M. Borzdyka's suggestion may be termed thermal brittleness. Two types of thermal brittleness are distinguished. Brittleness of the first type consists in a sharp drop in the impact ductility of the steel (more accurately, in elevation of

the critical temperature of brittleness) as a result of prolonged heating within a definite temperature range, even without load; this is not accompanied by modification of the other mechanical characteristics and physical properties of the steel. Thermal brittleness of the first type is a fully reversible phenomenon. The kinetics of its development do not differ from the kinetics of development of reversible temper brittleness. Alloying elements affect it in the same direction as they do temper brittleness. These circumstances, as well as the similarity in a number of other manifestations, permit the assumption that the nature of thermal and reversible temper brittleness is the same. The fact that the development of thermal brittleness is intensified under the effect of load cannot alter this thesis. According to our assumptions concerning the nature of thermal brittleness (see p. 280 and [57]), this may be ascribed to the fact that plastic deformation accelerates formation of the δ phase in the boundary layer of the grain. In fact, it has been established by experiment [10] that only such static stresses as are capable of causing appreciable creep in steel may accelerate the development of thermal brittleness. On the other hand, if loading causes no substantial plastic deformation, it also has no effect on the process of embrittlement of steel with time. The thermal brittleness is manifested in elevation of the critical temperature of steel embrittlement. The danger of failure of a part under immediate effect of the service temperature due to thermal brittleness of the first type may be ignored, however.

Thermal brittleness of the second type consists in a sharp drop chiefly in elongation and reduction in area of the steel as a result of prolonged heating under load. Hence I. H. Borotzka proposes [10] that brittleness of this type be termed "static thermal brittleness" to distinguish it from thermal brittleness of the first type, which he designates as "impact brittleness". It has also been suggested [54] that brittleness of this type be called "thermal weakening", since a drop in impact ductility (Fig. 324) and ultimate

strength is observed in this case as well. It seems to us, however, that it is not advisable to call this effect thermal brittleness at all, since it is the result of processes which cause intercrystalline failure along the right-hand branch of the stress-time to failure line (Fig. 302c). These processes depend not only on the temperature, but to no less an extent on the duration of load action and the magnitude of stress. The nature of these processes (the assumptions, including ours, as to their nature were discussed on [Russian] p. 304) differs from that of thermal (and temper) brittleness. If this phenomenon is nevertheless considered to be one of the types of thermal brittleness, then irreversibility should be regarded as its basic distinguishing feature. It has been demonstrated [846], it is true, that up to a certain test-period length the impact ductility can be restored by heat treatment and that a certain improvement in plasticity and toughness is also achieved by applying heat treatment in different stages of heating under load. But if the steel has been heated under load in excess of a definite period, heat treatment no longer improves either the impact ductility or the other properties, apparently because in this case the drop in plasticity and ductility is the result of local failures, i. e., the formation of fine cracks in the materials. It thus seems to us that it is advisable to designate thermal brittleness of the second type as "irreversible thermal brittleness".



Figure 324. Impact ductility at 20° of chromium-nickel-molybdenum steel after prolonged load application at 480° to 500° and $\sigma = 30 \text{ kg/cm}^2$ (Zibel' and Vellingar)
 o - 480°; • - 500°; (a) a_k , kg/cm^2 ; (b) duration of load application, hours.

But reversible brittleness caused by the prolonged action of temperature itself is also inevitably superimposed on irreversible brittleness in a number of steels. This may in turn facilitate the occurrence of cracks along the grain boundaries due to lowering of the tear resistance. Heat treatment employed before the appearance of cracks in the steel, as well as frequently repeated holding under load at various stages, apparently, increase the time to failure to a considerable extent by eliminating the reversible thermal brittleness which has developed by this time. This is also attested by the fact that heat treatment (high temperature anneal) yields the greatest effect in steels which possess increased sensitivity to reversible thermal brittleness.

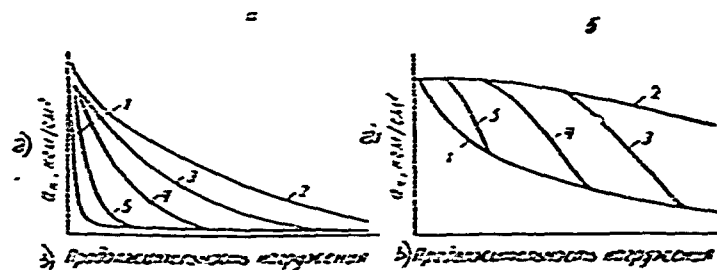


Figure 325. Diagram of effect of preliminary load application at 500° on impact ductility at 20° of steel sensitive (a) and only slightly sensitive (b) to embrittlement:

1 - fractured specimen; 2 - after load application

at $\sigma = 10 \text{ kg/mm}^2$; 3 - same at $\sigma = 20 \text{ kg/mm}^2$;

4 - same at $\sigma = 30 \text{ kg/mm}^2$; 5 - same at $\sigma = 40 \text{ kg/mm}^2$;

(a) a_k , kg-cm/cm^2 ; (b) duration of load application.

The diagram, borrowed from Fun and Rikhard [849] and shown in Figure 325, of change in impact ductility versus duration of load application at various temperatures for steels which are highly and only slightly sensitive to reversible thermal brittleness permits the assumption that for the former (chromium-nickel-molybdenum steels in particular) the chief cause of the sharp drop in impact ductility after prolonged load application at an elevated temperature (cf. Fig. 324) is reversible thermal brittleness, the development of which is

greatly fostered by the service stress. A question arises, however: why is it that for a number of steels which are only slightly sensitive to reversible thermal brittleness the sharp drop in plasticity and intercrystalline failure (i. e., irreversible thermal brittleness) is nevertheless accompanied by only a slight drop in impact ductility at room temperature in the event of prolonged load application at high temperatures? This may be ascribed to two circumstances. On the one hand, according to our assumption (Russian p. 506), "separation" of the grains, which still does not constitute cracks in the initial and middle stages, at least not on all boundary layers, takes place in this case. In this, in our opinion, lies the second reason that intermediate heat treatment is still capable of restoring the properties. On the other hand, processes of globular formation and coagulation of the carbides also proceed at the same time during prolonged load application at elevated temperatures, this leading to increased impact ductility at room temperature. It is true that plasticity also increases as a result of these processes, but it is not utilized at the test temperature, since the grains themselves scarcely undergo deformation.

In consequence of the different nature of the two types of thermal brittleness, alloying elements and other factors may exert a different effect on their development. In particular, irreversible thermal brittleness is intensified in an oxidizing medium, apparently in consequence of oxidation of the weakened grain boundary layers. Hence the sensitivity of steel to irreversible thermal brittleness decreases when it is alloyed with elements which raise its heat resistance. Thus, according to certain observations silicon and aluminum exert a positive effect. Increased heat resistance is probably also one of the important reasons that steels containing 5 to 6% Cr are less sensitive to irreversible thermal brittleness and that this effect is hardly observed in high-chrome steels. With the heat resistance practically identical, the sensitivity of a steel to irreversible thermal brittleness must, as a rule, be reduced by

alloying elements which increase its creep resistance under conditions in which diffusion plasticity mechanisms predominate, since both are achieved owing to the strengthening of the interatomic bond and greater orderliness of the grain boundary layer. Such elements include molybdenum, vanadium, titanium, and niobium, in particular. But it follows from the foregoing that alloying elements may have a different quantitative, and even qualitative effect on the sensitivity of steel to irreversible thermal brittleness and its creep resistance, if these elements are contained in the steel in a combination such that the latter acquires a great tendency toward reversible thermal brittleness, especially under the simultaneous action of a load. Chromium-nickel-molybdenum steel may serve as an example.

The chemical composition and the most important properties of the principal thermally stable pearlitic and ferritic-martensitic steels employed in Soviet and foreign boiler and turbine construction may be found in the reference and periodical literature¹ [756, 859, 912, 761, et al.] Carbon steels, widely used because of their cheapness and good technological properties, especially for steam pipes and steam superheater pipes up to 425 to 450°, occasionally up to 480°, possess a number of shortcomings. To say nothing of their low heat resistance and corrosion resistance, they are prone to graphitization, which is manifested chiefly in the seam zone of welded joints. They are also sensitive to mechanical aging and thermal brittleness.

Molybdenum steels of the 15M, 20M, and 16M types, which contain about 0.5% Mo and varying amounts of carbon, are the least alloyed of the alloy steels. Molybdenum steels possess a higher creep resistance and greater corrosion resistance than do carbon steels and are not sensitive to thermal brittleness. However, they are also not fire resistant and are still prone to graphitization. In conditions of long service at 500° and above they are

¹For their application to long service life, see also the bibliographic reference in the footnote and the text to which it refers on [Russian] p. 570 and [916].

insufficiently stable as well¹. Hence they have of late begun to supplant steel of the 12MKh type [1317], which contains 0.9 to 0.16% C, about 0.5% Mo, and 0.5% Cr. Additional alloying with chromium, as previously pointed out, prevents graphitization and at the same time increases the corrosion resistance somewhat as compared with molybdenum steel without chromium.

The largest group of pearlitic thermally stable steels are steels alloyed with chromium, molybdenum, niobium, vanadium, tungsten, and titanium. The chemical composition of certain of these steels is given in Table 91. An increase in the chromium content, is accompanied by a rise in the heat resistance and corrosion resistance of these steels. The Kh5M steel (Table 91) is frequently used semi-heat-resistant. With respect to thermal stability, on the other hand, particularly with respect to creep resistance, a steel with ~ 2.5% Cr and an identical percentage of the other elements, such as the Groley-2 steel (Table 91), is scarcely inferior to five-percent chromium steel [445]. The 25Kh2MFA steel (Table 91) possesses a high relaxation resistance, in consequence of which it is employed for fastening parts with a lengthy service life at temperatures up to 500°. It is accordingly recommended that it be tempered at 630 to 650° [136]. The EI454 steel (Table 91), which is alloyed with an increased amount of molybdenum and niobium, possesses adequate thermal stability up to 550°. The EI531 steel (Table 91), which contains less molybdenum but which is additionally alloyed with vanadium, is approximately equivalent to the EI454 grade at such temperatures.

As was noted at the beginning of the chapter, the pearlitic thermally stable steels possess a number of advantages, but a lower heat resistance, than the austenitic ones. Hence an important direction of subsequent research in this field is the development of steels possessing a high heat resistance

¹See, for example, I. L. Mirkin and M. I. Solonovs. *Metallovedeniye i obrabotka metallov* [Metallurgy and the Treatment of Metals], No. 2, 1957, p. 11.

which still retain a certain amount of austenite steels at service temperatures up to 600 to 650°C. Interesting results have been obtained with steels alloyed with titanium and boron. Thus, for example, a steel with 0.15% C, 3% Cr, 1% Mo, 0.05% Ti, and 0.01% B tested for the long-term strength and creep resistance values for 1000 hours at 650°C was found to approximate the 18-8 austenitic chromium-nickel steel [73b]. Positive results have also been obtained with chromium-molybdenum steel with 0.2% C, 1.5% Cr, and 0.5% Mo additionally alloyed with about 0.7% V [73c]. After normalizing at 930°C and tempering at 650°C, its 1000-hour long-term strength at 600°C is about 24 kg/mm^2 with an elongation of 5%. Gas turbine disks with a short service life at temperatures up to 600°C are manufactured from it in the USA. One of the most noteworthy of the low-alloy steels is the EI579 [Fe(C)Mn-10] (Table 9a). This steel was developed in Germany and employed there during the war (with a somewhat lower vanadium content) for such important articles as the turbine shaft of a jet aircraft. The best combination of properties was found in steel of this type in a number of later studies as well, in consequence of which it is employed, for example, for the rotors of stationary steam turbines, gas turbine disks with a short service life, bolts subjected to temperatures of around 600°C, etc. [73d, 859, 739, et al.].

Another direction of the research being conducted in European countries in the field of pearlitic thermally stable steels has the aim of lowering or eliminating the molybdenum content of the latter. One of the methods of achieving this aim also consists in using vanadium. In particular, chromium-vanadium, chromium-manganese-vanadium, and certain other steels were developed and employed (for molded castings as well) in Germany as substitutes for thermally stable steels even before the war, and especially during the war. Certain molybdenum-free steels alloyed with vanadium have recently been studied after long service (8,000 to 125,000 hours) at a moderate temperature of 500°C in Czechoslovakia [74-0] and have been found to be practically equivalent to

Chemical composition, % of certain elements and composition, % of the metal

No. of steel	Designation of steel	C	Mn	P	Cr	Mo	W	Ni	Other
1	15KhN	0.09-0.15	0.4-0.7	0.17-0.37	0.8-1.1	0.40-0.85	-	-	-
2	20KhN	0.15-0.25	0.4-0.7	0.17-0.37	0.8-1.1	0.15-0.25	-	-	-
3	30KhN	0.25-0.35	0.4-0.7	0.17-0.37	0.8-1.1	0.15-0.25	-	-	-
4	25Kh2NFA (ET10)	0.22-0.29	0.4-0.7	0.17-0.37	1.5-1.8	0.50-0.70	0.15-0.30	-	-
5	Cruby-2	0.15	-	0.4-0.7	1.8-2.5	0.5-0.7	-	-	-
6	El45b	0.12	0.4-0.7	0.4-0.7	2.1-2.6	0.8-1.0	-	1.3	-
7	El571	0.12	0.4-0.7	0.4-0.7	2.1-2.6	0.5-0.7	0.2-0.35	1.3	-
8	El750; FK(D) H-10	0.13-0.24	-	-	3.0	0.5	0.75	-	-
9	Kh1M	0.16	0.6	0.5	4.0-6.0	0.3-0.6	-	-	-
10	12Cr, Mo	0.15	-	-	11.5	3	-	-	-
11	Lapalloy	0.20	-	-	11.5	2.75	0.25	-	-
12	El756, El757; 12Cr, W, H1.	0.12-0.17	-	-	12-14	0.5	2.5-4.5	-	1.8 Ni
13	12Cr, Mo, W, V	0.16-0.23	-	-	11.5-13.0	0.9-1.1	0.8-1.2	0.16-0.27	0.8-0.8 Ni
14	El900, ReX408	0.10-0.20	-	-	10-13	0.6-0.9	0.10-0.20	0.3-0.6	1.5 Ni

* The following more exact specification of the composition has been projected:
0.03% C, 0.12% Cr, 0.3% Mn, 0.6% Si, 0.7% Ni, 0.9% Nb.

the molybdenum steels. A molybdenum-free steel containing 0.25 to 0.50% C, 1.2 to 1.4% Cr, 1.0 to 1.4% Ni, and 0.2 to 0.5% V has been recommended in the Soviet Union for the manufacture of fastening parts intended for lasting service at temperatures up to 500° [74]. According to the data of the authors, with respect to the aggregate of the properties it is equivalent to the 25Kh2NFA steel (Table 91) and is superior to the 30KhMA steel.

Ferritic-Martensitic Steels

High-chromium steels with 12% Cr, 17% Cr, 25% Cr, and 28% Cr (in the Soviet Union, brands Kh13, Kh25, Kh25T, Kh28) are employed chiefly where their high corrosion resistance and heat resistance may be utilized. With respect to thermal stability, particularly creep resistance, they are inferior to low-alloy steels: the creep strength of the Kh13 steel drops sharply after 450°, and that of the Kh25 steel even more so. The Kh13 and Kh25 steels are employed chiefly for springs, particularly for flat sealing springs in steam turbines in service for long periods at temperatures up to 400°¹.

The Kh13 and Kh25 stainless twelve-percent chromium steels are widely used for the manufacture of steam turbine vanes for operation at temperatures up to 480°. This is favored by their high resistance to corrosion and scale formation, good technological properties, and high mechanical properties in the refined condition. An additional important property of these steels applicable to the purpose in question is their great capability of damping elastic vibrations (high damping ratio), although this property was not taken into account when the steels were introduced for this purpose, since it was established later.

An abnormally high damping ratio is inherent in ferromagnetic metals

¹The B18 high-speed steel has been recommended for the manufacture of springs designed for a long service at 470° [742] (it is occasionally also employed for springs intended for service at temperatures up to 400°). Positive results have been yielded by a test heat steel with 0.5% C, 2.1% Cr, 1% Mo, 0.4% V (footnote continued on page 87)

and alloys in the non-magnetized state. This is explained by the fact that the magnetization vectors in the domains are oriented by stresses in the direction of easy magnetization, which is near the direction of the acting force, and a magneto elastic hysteresis occurs upon vibration. Hence the energy losses per cycle and the attenuation ratio are proportional to the residual magnetostriction of the material. It is to be seen from Figure 326 [440], in which are shown the domains of binary and ternary ferromagnetic alloys which possess high and relatively high residual stress γ_r values, and accordingly high and relatively high damping ratio values as well, that the latter usually drops when the alloy is alloyed with chromium. However, a binary iron alloy with $\sim 12\%$ Cr possesses a relatively high damping ratio (for the other alloys in Figure 326, see [Russian] p. 575). The maximum damping tendency is also observed in steel when it contains about 12% Cr, as may be seen from Figure 327 [478], where this property is expressed as "specific damping tendency", which is the ratio of the energy lost per cycle to the maximum energy per period. With elevation of the service temperature, as is to be seen from the example given in Figure 328 [762] for 1Kh13 steel, the attenuation ratio decreases, this being due to a drop in magnetostriction. Above the Curie point it has low values, since the domains disappear and the material becomes paramagnetic.

It was established long before the war that the creep resistance of twelve-percent chromium steel at temperatures above 500° may be appreciably increased by the additional introduction into it of about 3% W or up to 2% Mo. Extensive research of additional alloying of twelve-percent chromium steel

(Footnote continued from p. 86)

(EI725 steel). A check of specimens from an industrial heat have demonstrated the suitability of this steel for flat springs for service at 470° and even at 500° . This steel has also exhibited (cf. Metallovedeniye i obrabotka metallov, No. 12, 1956, p. 17) a high relaxation resistance at 500 to 550° and has been recommended for the fastening parts of steam turbines with high and extra-high steam parameters. Steels have recently been developed (EI612, EI673, the EI765 alloy; T. I. Volkova, Metallovedeniye i obrabotka metallov, No. 6, 1956, p. 21) for springs designed for service at 585 and 640° .

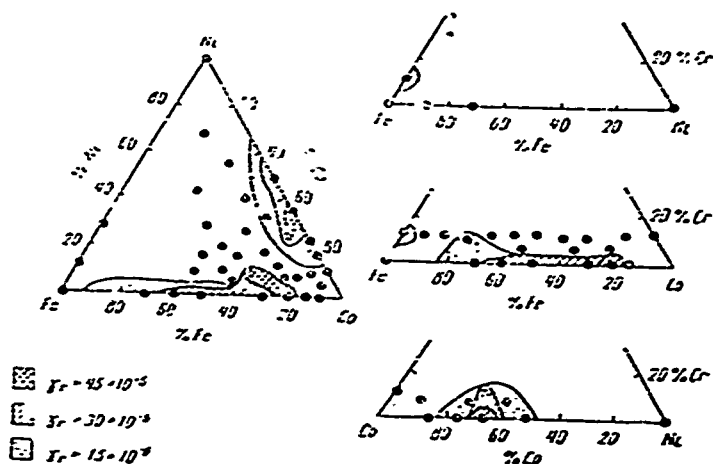


Figure 526. Capability of pure binary and ternary ferro-magnetic alloys of iron, cobalt, nickel, and chromium, of damping vibrations.

with various elements has been conducted during the post-war years with the aim of expanding the temperature range of possible utilization of ferritic-martensitic steels in place of austenitic steels at temperatures up to 550-600°. Examples of steels of this type which have been put to industrial use are given in Table 91 (steels 10 - 14). It may be seen from the table that the average carbon content in these steels does not exceed 0.15 to 0.20%. The creep resistance drops in the event of a higher carbon content. Steel 14 (Table 91) which is employed for gas turbine vanes and disks, has the greatest heat resistance at 600° and with a service life of up to 1000 hours. However, the industrial employment of such steels is hampered in certain fields (the chemical industry and others) by the fact that they are much inferior to austenitic steels as regards weldability.

Steels with 0.15 to 0.20% C and 12% Cr additionally alloyed either with 0.6% Mo and 0.3% V or with 1% W and 0.3 V have been recommended in the Soviet Union for turbine vanes and other parts with a service temperature up to 550 to

560° and a long service life, on the basis of the preliminary results of study of industrial pilot-lots of blanks [762]. These steels, with their higher heat resistance than the 12h13 and 21h13 steels without additional alloying, are not inferior to the latter with respect to the values of the most

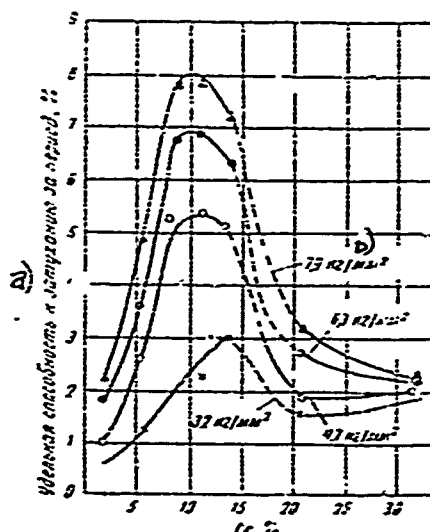


Figure 327. Effect of chromium content of steel on its capability of attenuating vibrations.

(a) specific attenuation capability per period, %;
(b) kg/mm².

important physical properties, particularly the magnitude of the damping ratio at temperatures of 20 to 550°. Steels of similar composition (the EI747, EI748) have been recommended¹ for parts designed for service in power plants with a steam temperature at the inlet of 565 to 600°.

Figure 329, which is based on the data of Soviet research [743] illustrates the effect of titanium, niobium, and tungsten on creep resistance at 600° of a steel the matrix of which contains 0.10 to 0.15% C, 10 to 12% Cr, 0.6 to 0.8 Mo, and 0.2 to 0.3% V. With a higher vanadium content, as this same research has shown, the heat resistance of high-chromium steel drops, in contrast to that of low-alloy steel. It is to be seen from Figure 329 that titanium is not effective and that niobium has a positive effect, but that the creep rate drops the most sharply in the event of a content of about 4% W.

¹E. S. Ginzburg. *Metallvedeniya i obrabotka metallov*, No. 5, 1956, p. 47

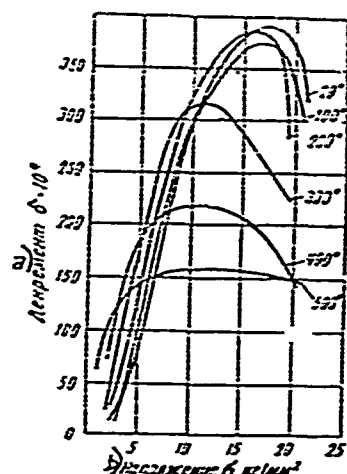


Figure 328. Change in vibration attenuation ratio of 1Kh15 steel with elevation of temperature.
(a) attenuation ratio $\delta \cdot 10^4$;
(b) stress σ , kg/mm².

With this tungsten content the steel also possesses the greatest long-term strength and preserves satisfactory plasticity and impact ductility values after very long exposure to high temperature. Hence the authors recommend two steels comprising the matrix referred to above, additionally alloyed with 4% W (EI757 steel) and 2% W (EI756 steel), for industrial testing as a material for steam turbine vanes or service at 550 to 600°. A steel additionally alloyed with 4% W and 0.4% K simultaneously has a somewhat higher heat-resistance, but this steel has almost exclusively a ferritic structure and a low impact ductility. With respect to its tendency toward the development of brittleness during protracted heating, the EI757 steel must also be inferior to the EI756 steel.

A steel conditionally designated 15Kh12VWF (EI802) and additionally containing 0.8 to 0.9% W, about 0.5% K, and 0.2% V, besides 12 to 13% Cr is recommended in another study [744] for extensive service at 550 to 600° as a material for the vanes of steam and gas turbines, disks, etc. A steel designated 15Kh12WF into which 0.6% K and 0.2% V are introduced has lower properties. It is thus intended for service at lower temperatures than the first one named.

Certain negative features are inherent in high-chromium steels. One of these consists of the fact that steels which are ferritic with respect to

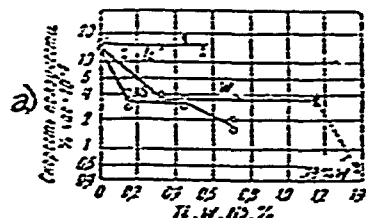


Figure 329. Effect of titanium, niobium, and tungsten on the creep resistance of a steel with 0.10 to 0.15% C, 10 to 12% Cr, 0.6 to 0.6% Mo, and 0.2 to 0.3% V at 600°.

(a) Creep rate, %/hour $\cdot 10^{-5}$.

their chromium and carbon content have an extremely coarse primary grain and are highly prone to coarsening of the grain in the process of their service, at temperatures above the recrystallization point, it not being possible to refine by heat treatment the coarse grain obtained in them. A coarse primary grain is also observed frequently in partially ferritic high-chromium steels.

Effective refinement of the grain of an ingot or castings of such steels is achieved upon the introduction into them of a small quantity of nitrogen (usually of nitrated ferrochromium) or titanium, calcium, and certain other elements. The addition of a few hundredths of one percent of titanium or vanadium has no effect on primary crystallization [105]. As demonstrated by a study of V. N. Svechnikov and H. S. Alferova [458], the introduction of titanium in the amount of 0.35% very sharply refines the grain in a cast alloy. The introduction of niobium (0.5 to 2.0%) or tantalum (1 to 1.5%) has a slight effect. An effect sufficient for practical purposes is achieved by the introduction of titanium in the steel in an amount up to 0.1 to 0.15%, and an even better effect by simultaneous blowing down of the metal prior to tapping with commercially pure nitrogen or with air [77].

However, different elements, including nitrogen, refine the grain chiefly on when the pouring temperature is not too high.¹ This creates serious difficulties in the manufacture of rolled castings from high-chromium steels,

¹The pouring temperature was not indicated in the study by Svechnikov and Alferova and apparently was not taken into account. Hence it is possible that in reality the arrangement of the elements according to the effectiveness of their action on refining the grain in a casting differs somewhat from that obtained by them.

since the metal must be superheated for better filling of the mold, the more so since the admixtures themselves, particularly titanium and nitrogen, which are the most effective, impair the flowability appreciably [496]. For this reason efforts are being made to introduce into high-chromium steels elements which improve their flowability. An increased content of silicon, which also increases the heat resistance, is useful in this respect. It must be borne in mind in this case that silicon contributes to appearance of the α -phase.

As regards the tendency of the grain to growth in high-chromium steel at high service temperatures, according to research by the author and Yu. M. Margolin [105], it diminishes appreciably when as little as a few hundredths of one percent of vanadium or finely crushed chamotte is introduced in the steel. Thus, in a steel with 28 to 30% Cr and 5% Al without additions, coarse crystals are formed at 1100° even after two-hour holding, and in the event of holding for 54 hours or over the entire specimen consisted of two to three crystals; in the same alloy with an admixture of 0.05% V, large crystals appeared only upon holding for 52 hours. V. E. Svechnikov and M. S. Alferova divide the elements studied by them [458] into three groups: (1) those which greatly retard grain growth (in a steel with 28% Cr): niobium, tantalum, titanium, and nitrogen (2) those which retard grain growth only at temperatures up to 1100°: vanadium and molybdenum; (3) elements which have no effect on grain growth: tungsten, cobalt, nickel¹, beryllium, selenium, and tellurium. In their opinion titanium, niobium, and tantalum have the greatest effect because they form independent stable carbides which are dissolved in the cementite. When the steel is heated below 1200°, nitrogen retards grain growth because of the formation of dispersed nitrides, and above 1200° because of the appearance of a large quantity of the gamma phase. An admixture of the oxides

¹There are data, however (D. I. Odesskiy and V. M. Vozdvizhenskiy, Metallovedeniye i obrabotka metallov, No. 9, 1957, p. 42), indicating that the introduction of up to 2% Al simultaneously with 0.2% N into Kh28 steel impedes grain growth and contributes to achievement of a favorable weld joint structure.

of rare-earth elements has been used in England in recent years with the aim of reducing grain growth [172].

A second negative property of high-chromium steels is the high critical brittleness temperature, which causes a low impact ductility at room temperature. The impact ductility of these steels drops sharply starting at 18 to 20%, at their normal content of 0.15 to 0.20% C, this usually being ascribed to the ferritic structure and coarse grain. A substantial rise in the ductility of conventional melt steels is achieved by the introduction of about 0.15% N into them. Research in recent years [838] has shown, however, that melting in vacuo yields a far greater effect. As may be seen from Figure 330 [851], for steels melted in vacuo the critical brittleness temperature drops from 65° with 12% Cr to -130° with 25% Cr (Fig. 330a). The impact strain at room temperature is at the maximum with 26%, but still retains high values up to 35% Cr (Fig. 330b). For the sake of comparison we point out that for a steel with 25% Cr of the conventional melt, the impact strain is about 5 foot-pounds ($a_k < 1 \text{ kg/cm}^2$). Certain investigators ascribe the drop in the brittleness temperature to decrease in the carbon and nitrogen content and the rise in the absolute impact ductility values to decrease in the content of oxygen (oxides). According to the data of the authors of [851], in order to obtain the properties shown in Figure 330, the total percentage of carbon and nitrogen in a steel with 25% Cr must not exceed 0.035%, and 0.055% in a steel with 16% Cr. It is interesting to note that the grain of steels melted in vacuo is several times as coarse as that of industrial steels. This confirms once again the fact that the low-hardness phases formed in the boundary layer of the grain by harmful impurities have a much greater effect on the cold shortness than the coarse grain itself. But the effect of a coarse grain on conventional melt steel is, of course, negative.

Hence any factor favoring coarsening of the grain must be prevented with especial care in high-chromium steels. Such factors include above all too high

a heating temperature for rolling (above 1100°) and temperature at the end of rolling (above 850°) [cf. 854]. Thus, with thick sheets of high-chromium steels one can obtain a relatively fine grain (sizes 4 - 5), an elongation of over 20% (with the Kh25T and Kh28 steels), and an impact ductility of over 3 kg-cm^2 (with the Kh25T steel), if the rolling of the slabs is conducted in the $980-1000^{\circ}$ to $720-800^{\circ}$ range with air cooling of the sheets, and the sheets are subjected to high temperature anneal in the pile at 760 to 760° for 12 to 16 hours, and then to water-quenching sheet by sheet from the same temperature.¹

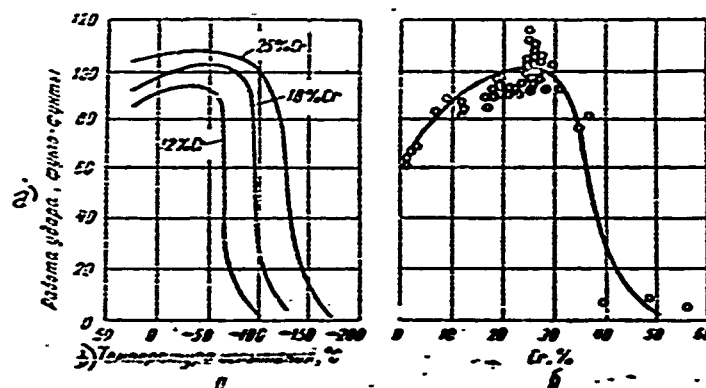


Figure 530. Effect of chromium on critical brittleness temperature (a) and impact ductility at 20° (b) of Fe-Cr alloys melted in vacuo.

(1) impact strain, foot-pounds; (2) test temperature, $^{\circ}\text{C}$.

A third serious disadvantage inherent in high-chromium steels containing over 15% Cr, as well as in heat-resistant Fe-Cr-Al alloys lies in the fact that if they have been exposed at 400 to 550° for a long period, they become brittle after cooling to room temperature: their impact ductility and plasticity fall almost to zero. In a steel with 27% Cr, brittleness develops even after holding for an hour at 475° and it becomes completely brittle after holding for 50 hours. This phenomenon, which is termed "475-degree brittle-

¹ G. A. Babakov, P. A. Zhadan, V. A. Danilin, S. F. Bakunin, E. I. Antipov, M. E. Kul'kov, and S. Z. Kupryakhina. *Stal'* [Steel], No. 6, 1957, p. 555.

ness" in the American literature, is not related to thermal or temper brittleness, since it is accompanied by different modifications of a number of the properties of the steel. The hardness (and ultimate strength) of the steel rise slowly and after holding for several thousand hours may become double that in the initial state. The resistivity, coercive force, magnetic saturation, and specific gravity undergo considerable change. Steel in the brittle state is etched more rapidly and corrodes many times more rapidly than normal steel of the same composition. The process causing 475-degree brittleness is completely reversible: all the properties of the steel are restored after heating for one hour at 600 to 650° with subsequent rapid cooling. If the steel is in service at temperatures above 650°, in order to prevent "embrittlement" of it as it passes slowly through the 400 to 550° range during periodic coolings, the latter must be conducted at an accelerated rate.

Additional alloying of ferrochromium alloys with other elements such as carbon, silicon, titanium, niobium, etc., does not weaken the process which causes brittleness in these alloys. The elements which form stable carbides or nitrides even intensify this effect somewhat, apparently because the solid solution contains more chromium in this case. Only nickel, and especially manganese, have a certain positive effect. Thus, when ~3% Mn is introduced into the steel, the process is retarded and the amount of chromium below which the effect described is not observed increases from ~15% to ~17%.

The 475-degree brittleness apparently also explains the drop, observed by N. S. Alferova [65], in impact ductility (and in a steel with 27% Cr, the plasticity as well) which is accompanied by elevation of the ultimate strength for steels with 17% Cr and 27% Cr after cold plastic deformation and subsequent quenching from 500°. Additional alloying of 27-percent chromium steel with titanium or niobium did not eliminate the drop in its impact ductility after the treatment indicated.

The nature of 475-degree brittleness, despite the numerous studies [cf. 74], for example, has not yet been ascertained. The nature of the modi-

modification of the properties of the steel which accompanies this effect apparently bespeaks the precipitation of a certain phase from the solid solution. But the composition of this phase has not been established. Certain investigators consider it to be the sigma phase. This is contradicted, however, by the nature of modification of a number of the physical properties of the steel, particularly the increase in magnetic saturation after holding at 475° . The alloying elements, especially manganese and nickel, also affect the 475° -degree brittleness differently than they affect formation of the sigma phase. Finally, work hardening, which greatly accelerates formation of the sigma phase, has a fainter effect on the development of brittleness at 475° . The majority of investigators conclude that the submicroscopic phase precipitated is a solid solution, possibly ordered, which is rich in chromium. The hypothesis has also been advanced that it has a Fe_3Cr composition. The sigma phase, coexisting with the phase of unknown composition, was also observed after holding at 475° in an intensively work hardened steel with 27% Cr.

Another form of brittleness which occurs in high-chromium steels in the event of their protracted heating in the 600 to 800° is actually related to formation of the sigma. The sigma phase will be treated in greater detail during the discussion of austenitic heatproof steels (Russian p. 560).

An interesting effect of importance for practical purpose has been detected in twelve-percent chromium stainless steel of the 2Kh15 type. As has already been pointed out (see Fig. 327), this steel possesses a high damping ratio. However, as a result of lengthy service, specifically 12,000 hours at a temperature of around 150° (for the ninth stage, in which the effect was detected), the damping ratio drops sharply, this leading to failure of the vanes. After heating at 650 to 680° with subsequent air cooling, the damping ratio increased $\sim 50\%$ at a stress of 12.65 kg/mm^2 , and at a stress of 25.3 kg/mm^2 , its increase reached 150% [460]. The authors ascribe this phenomenon to the circumstance that hardening occurs in the individual grains in the pro-

cess of cyclic action on the material of the vane. The extent of this hardening increases with increase in the number of cycles, while the service temperature of around 150° contributed to further hardening as a result of mechanical aging. An additional cause of drop in the damping ratio, according to the authors, could be precipitation hardening due to precipitation of highly dispersed particles of the sigma phase; this, however, is scarcely probable at 150° in a steel with 12% Cr, even in the event of service for 12,000 hours. Moreover, in the vanes studied by the authors, the impact ductility was greater than 7 kg/cm^2 , with $\sigma_s > 50 \text{ kg/mm}^2$, $\sigma_b > 70 \text{ kg/mm}^2$, $\delta > 16\%$, and $\psi > 60\%$. This phenomenon requires further study.

The silchromes, i. e., steels alloyed with chromium and silicon, have become widespread in all countries as heat resistant and thermally stable steels. Steels alloyed with chromium, silicon, and aluminum (the sichromals), which are employed chiefly in Germany, were also recommended at one time in the Soviet Union. However, the sichromals, which have a complex composition, possess a low creep resistance along with their relatively high heat resistance. This is also true of the chromium-aluminum steels, which are thus employed chiefly as heat resistant high-resistivity alloys for heater elements. Of the sichromals, a certain use is made at the present time in the Soviet Union chiefly of the Kh12YuS steel, with 1.2 to 2.0% Si and 1.0 to 1.8% Al, as a heat resistant steel up to 900° under reduced load. A semi-ferritic steel with 0.06 to 0.1% C, 6% Cr, 1.5% Si, and 0.9% Al is also used.

It has been demonstrated in recent studies [76], however, that the heatproof quality of a steel with 25% Cr and 5% Al may be greatly increased by additional alloying with tantalum, its very high corrosion resistance being retained. Thus, the introduction into such steel of 5% Ta raises the 100-hour long-term strength at 1200° from 0.7 to 2.2 kg/mm^2 and the introduction of 10% Ta raises it to $\sim 4 \text{ kg/mm}^2$. Replacement of 5% tantalum by niobium reduced the long-term strength to $\sim 2 \text{ kg/mm}^2$, but the creep resistance

remained the same. Alloying with other elements simultaneously with the tantalum produced no effect.

Interesting prospects for industrial use as heatproof alloys at temperatures up to 650 to 700° have recently been discovered for ferroaluminum alloys [764], the plasticity of which may be sharply increased by melting in vacuo owing to the great drop in the oxygen content. The plasticity of such alloys begins to drop only with $\sim 10\%$ Al, while that of conventionally melted alloys begins to drop even with 2 to 3% Al. In vacuum melted alloys with 10% Al the elongation is still around 35% . An alloy with 8% Al additionally alloyed with 3% Ti is only slightly inferior to the 18-8 austenitic steel with respect to the 100-hour long-term ultimate strength up to 675° , and an alloy with 14% Al and 3% Ti was superior to this steel. Molybdenum is less effective in these alloys than in others, but according to available information [766] a ferrous alloy with 16% Al and 3.3% Mo melted in vacuo is employed (under the name "termenol") as a corrosion resistant alloy at temperatures up to 1260° . The superiority of ferroaluminum alloys over steel alloyed with nickel lies in their greater resistance to the action of media containing sulphur. There is also a report [764] of successful service of these alloys for 500 hours in carburizing and cyaniding furnaces.

In the silchromes the chromium content usually ranges from 6 to $10-15\%$. As regards the silicon, the chief aim of introducing it being to increase the corrosion resistance of the steel, its maximum quantity must be such that the steel retains the pearlitic structure and its capability of being hardened by quenching and tempering. The carbon content of the silchromes (except for the Kh6SM steel, which is not subjected to quenching and tempering) ranges from 0.35 to $0.5-0.6\%$, sometimes even up to 1% , for the same purpose. The function of chromium in increasing the short-term strength is especially pronounced at temperatures above 500° [462].

Molybdenum is introduced into certain silchromes in the amount of 0.5

to 0.6% in order to increase the thermal stability. Cobalt in the amount of 2% has a positive effect in this respect. However, the introduction of cobalt for this purpose is not worth while. The silchromes Kh6S, Kh6SX, Kh7CM, Kh9SP, and Kh20S2X are used in the Soviet Union (GOST 5632-51). The last two steels are employed chiefly for the bleeding valves of internal combustion engines operating at temperatures up to 750 to 800°. The Kh10S2 steel is not suitable for lengthy service at 550 to 600°. Its creep resistance and long-term strength also drop sharply at temperatures above 500°. Owing to its high relaxation resistance at 450°, it may be employed for fastening parts subjected to this temperature [cf. 756].

B. AUSTENITIC HEAT-RESISTANT STEELS

Matrix and additional alloying

As was demonstrated on [Russian] p. 511, austenitic steels possess better heatproof qualities than steels with a ferritic matrix. However, many austenitic steels cannot be utilized as heat-resistant steels due to the fact that their other properties do not meet the requirements set. Thus, pure-nickel austenite possesses a low heat resistance, pure-manganese austenite a low heat-resistance and corrosion resistance, poor machinability by cutting tools, etc. The principal alloying element which, depending on its proportion, imparts an increased or high heat resistance, even in austenitic steels, is chromium, the effect of which is illustrated by way of an example in Figure 551 [465]. Hence all heat resistant gamma alloys contain a certain amount of chromium.

Thus, the austenitic matrix of ferrous alloys must contain chromium (in an amount which is the greater, the higher, chiefly, is the heat resistance required of the alloy) and nickel and/or manganese. With increase in the amount of nickel, as has been established by a number of studies, there is an increase in the short-term strength. The creep resistance, on the other hand

remains practically constant, starting at a certain nickel content. Thus, it is to be seen from Figure 352a [579] that the unit creep stress at 600 and 700° for a steel with 20% Cr rises sharply until the Ni contents reaches approximately 10%, i. e., up to formation of an austenitic structure, after which the curve runs horizontally. At a percentage of 15% Ni, chromium (Fig. 352b) has a greater effect on the creep than does the nickel, but after 15 to 16% it also has a faint effect. It is to be noted, however, that the role of nickel is intensified when it is combined with other elements. Moreover, the advisability of increasing the nickel content may be conditioned by its effect on the other properties of the steel. However, this problem calls for further study.

The amount of nickel required for obtaining an austenitic structure depends on the steel's content of chromium and additional alloying elements introduced into it with the aim of improving the heatproof quality or corrosion resistance. When contained in a steel in an amount of up to 16 to 17%, chromium combined with nickel contributes greatly to achievement of an austenitic structure, in contrast to its usual ferritizing action. This is in our opinion the result of a complex interatomic interaction, the possible nature of which was discussed on pages 56 and 60. In a higher percentage, the chromium impedes achievement of an austenitic structure. This is illustrated by the structural diagram of Figure 355, which is based on the data of various investigators. The chromium content and the amount of the additional ferritizing element equivalent to the chromium are plotted along the axis of abscissae, and the amount of nickel required in this case to obtain austenite without the alpha phase along the axis of ordinates. Molybdenum is the additional alloying element in the case illustrated by Figure 355. The position of the steels 18-8, 16-15-3, and 16-25-6,¹ which contain less than 0.07% C,

¹In this system of symbols, the first set of figures designates the chromium content of the steel, the second the nickel content, and the third the molybdenum content, in percent values.

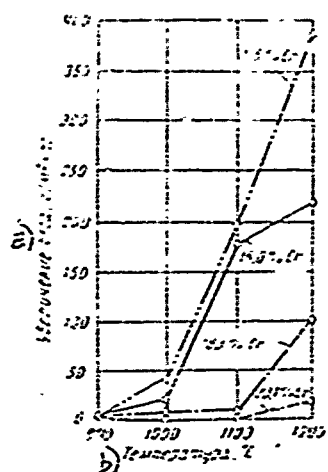


Figure 331. Effect of chromium on the corrosion resistance of austenitic steel with 14% Cr, 14% Ni, and 2% W.

(a) Weight increase, $\text{g}/\text{m}^2/\text{hour}$;
(b) Temperature, $^{\circ}\text{C}$.

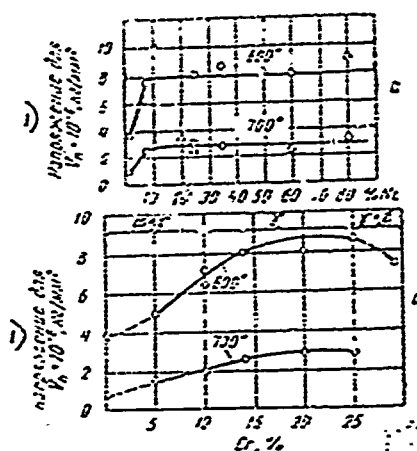


Figure 332. Effect of nickel at a percentage of 20% Cr (a) and of chromium at 15% Ni (b) on the creep resistance of chromium-nickel austenitic steel.

(1) stress for $\dot{\epsilon}_n = 10^{-5}$, kg/mm^2 .

is shown as an example in the diagram of Figure 333.

It is also to be seen from Figure 333 that, other conditions being equal, the amount of nickel necessary for obtaining stable austenite in chromium-nickel steel depends on the carbon content of the latter. The contents of chromium, nickel, and carbon are interrelated by the empirical relationship [466]

$$\frac{\text{Cr} - 16\text{C}}{\text{Ni}} \leq 1.7,$$

from which it follows, for example, that for 26% Cr and 0.3% C the minimum amount of nickel is 12.5%, while for 0.45% C it equals 11%.

Nitrogen has an effect in the same direction as carbon. Thus, for example, studies by A. M. Samarin et al. [470] demonstrate that in a steel containing 25% Cr the amount of nickel required for obtaining an austenitic structure is about 18% with a normal nitrogen content, but only 13% when 0.2 to 0.25% nitrogen is introduced into the steel. The possibility of replacing a portion

The numerous studies of the possibility of replacing nickel in the austenitic matrix by manganese have shown that chromium-nickel and chromium-manganese matrices are approximately equivalent, at least when other elements are additionally introduced into the steel. The studies of A. M. Borzdyks [464] and certain foreign authors show that chromium-manganese possesses better heatproof qualities than does chromium-nickel austenite, and only diphasic chromium-manganese steel containing 20 to 25% of the alpha phase is inferior with respect to heatproof qualities to single-phase chromium-nickel steel.

The superiority of chromium-manganese austenite is revealed more clearly after quenching from a temperature above 1000 to 1100°.

Manganese, just as nickel, has a slight effect on creep resistance when present in a quantity exceeding that required for obtaining an austenitic structure in the steel. The minimum amount of manganese with which a steel alloyed with chromium acquires an austenitic structure is highly dependent on the steel's carbon content. When the amount of carbon in a steel containing over 15% Cr is very low, it is impossible, as is to be seen from the structural diagram shown below in Figure 346b, to obtain a monophasic austenitic structure with any manganese content. With 0.3 to 0.4% C and 18% Cr, it is necessary to introduce over 12% Mn into the steel for this purpose. The effect of nitrogen is in the same direction as that of carbon in chromium-manganese steel, just as it is in chromium-nickel steel. When nitrogen is introduced in an amount exceeding 0.5%, a monophasic austenitic structure stable up to 1250° may be obtained in chromium-manganese steel when the latter contains 17% Cr, and when over 0.5% N is introduced, the same may be obtained in a steel with 16 to 17% Cr, 13 to 14% Mn, and 2.0 to 2.5% Mo [cf. 873, 765].

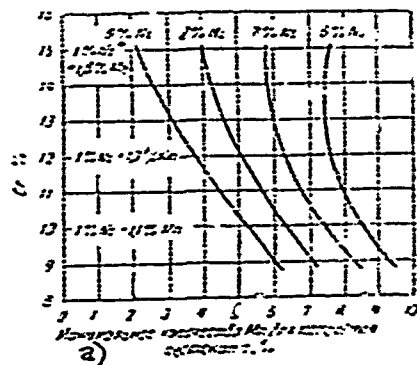


Figure 346. Structural diagram for chromium-manganese-nickel steels.
(a) minimum amount of Mn to obtain austenite, %.

Obtaining austenite is facilitated in the event of partial replacement of nickel by manganese. The amount of manganese required to impart a stable austenitic structure to steel alloyed simultaneously with chromium and nickel

may be taken from the structural diagram given in Figure 334 [466]. Thus, for example, with 6% Ni and 12% Cr, the minimum amount of manganese with which the steel possesses an austenitic structure is 5%, and with 15% Cr it is 4%. The amount of manganese equivalent to 1% Ni is smaller in the event of a low chromium content, as is shown by the diagram.

With the given manganese content the amount of nickel necessary for obtaining an austenitic structure decreases substantially, while with the given manganese and nickel content austenite may be obtained at a higher percentage of chromium (over 15%) if nitrogen is introduced into the steel. This is to be seen from the structural diagram given in Figure 335 [791] for chromium-manganese-nickel steels with 0.10 to 0.12% C and 0.08 to 0.15% N air cooled after heating for 15 minutes at 1575°.

The valve steels containing 0.37 to 0.45% C, 1.4 to 1.8% Si, 12 to 13% Mn, 14.5 to 15.5% Cr, and 2.0 to 2.5% W or 2.5 to 3.0% Mo, developed in our country at one time [467], and the Modern EI481 steel, which contains on the average 12.5% Cr, 8.5% Mn, and 6% Ni, as well as 1.25% Mo, 1.4% V, 0.6% Nb with 0.37% C, may serve as an example of heat-resistant steels with a chromium-manganese austenitic matrix in place of a chromium-nickel matrix. A steel designated as "chromadur" and containing on the average 12.5% Cr, 16% Mn, > 1.5% V, and 0.25% N was proposed during the war in Germany [cf. 469]. Steels have been developed in the USA [466, 895] in which nickel is partially replaced by manganese, particularly steels containing 10 to 12% Cr, about 2% Si, 4 to 10% Ni and accordingly 12 to 2% Mn (the exact amount of manganese depends on the nickel content in conformity with the diagram of Figure 334), as well as those containing over 15% Cr. Increasingly greater attention has been devoted of late, both here and abroad, to steels with a chromium-manganese-nickel matrix which contain over 15% Cr (see also [Russian] p. 606).

However, chromium-manganese austenite is inferior to chromium-nickel austenite with respect to corrosion resistance. Moreover, it possesses

a lower stability and greater tendency toward the development of brittleness during protracted service than does chromium-nickel austenite. This is explained to a large extent by the active participation of manganese in the process of carbide formation during prolonged heating [357, 362]. In the event of an increased carbon content of the steel, the active participation of manganese in the process of carbide formation may even be considered to be

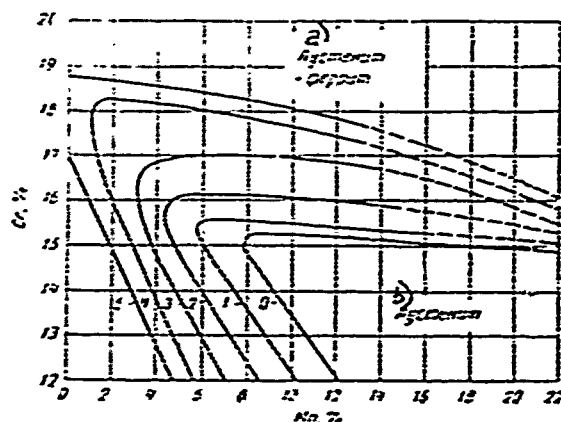


Figure 335. Structural diagram for chromium-manganese-nickel steels with 0.10 to 0.12% C and 0.08 to 0.15% N. The figures on the curves designate the nickel content, % (a) austenite plus ferrite; (b) austenite.

the basic cause of this shortcoming of chromium-manganese and chromium-manganese-nickel austenitic steels, in consequence of which they are suitable chiefly for brief period of service. Of interest in this connection is the use of nitrogen, owing to which it is possible to obtain austenite in chromium-manganese and particularly in chromium-manganese-nickel steel (the latter with a reduced nickel content). When it contains over 15% Cr, this increases the corrosion resistance. At a relatively small amount of carbon, this reduces the danger of development of brittleness during prolonged heating. In particular, in the 16-25-6 low-carbon chromium-nickel-molybdenum steel with nitrogen, it is possible (see [Russian] p. 367) to replace 10% nickel by 6% manganese. It is true that in steels containing nitrogen the development of

brittleness is intensified upon prolonged heating due to precipitation of carbonitride phases, but the negative effect of the nitrogen diminishes in the event of very long heating (see Fig. 339b).

The steels still used as the principal ones are those with chromium-nickel austenite, sometimes without additional alloying, but for the most part with additional alloying elements. Molybdenum, tungsten, niobium, titanium, cobalt, and boron are usually additionally introduced into them with the aim of improving the heatproof properties. Titanium and niobium at the same time prevent or reduce intercrystalline corrosion. Of the elements which can additionally increase the corrosion resistance, use is made in practice of silicon, since aluminum lowers the creep resistance somewhat and is less convenient from the metallurgical standpoint. Silicon also increases the dynamic strength of austenitic steel, both at room temperature and at temperatures up to $\sim 900^{\circ}$. This makes it an especially effective admixture in steels of the valve type. But aluminum is sometimes introduced in combination with titanium (cf. Table 94) in order to intensify the tendency toward precipitation hardening due to the complex σ' phase. Finally, the introduction of small additions of rare earth elements in the form of complex alloying elements or oxides in addition to an increased amount of manganese, into austenitic steels for the purpose of improving the technological properties, chiefly the deformability in the hot state, has begun in recent years.

In the additional alloying of heat-resistant austenitic steels, as well as alloys with other bases, the principle substantiated above of introducing several elements simultaneously in relatively small quantities has been adhered to with increasing frequency in recent years, particularly for the purpose of improving the heatproof qualities of the steels.

The carbon content of heat-resistant austenitic steels is usually determined by the method by which articles are manufactured from them. In deformable steels the carbon content normally does not exceed 0.2%, and in cast

steels it ranges from 0.3 to 0.45%. Only in cases in which the principle of aging by precipitation hardening of the carbide phase is applied in a deformable steel is the carbon content also increased to 0.4 to 0.45%. The effect of carbon on the heatproof qualities and the corrosion resistance was discussed earlier.

The most important shortcomings of heat-resistant austenitic steels

Austenitic steels, while having better heatproof qualities than pearlitic and ferritic-martensitic steels, at the same time possess a number of shortcomings. The latter include their low thermal conductivity and high thermal expansion coefficient. However, the thermal conductivity of austenitic steels, as is to be seen from Figure 336 [cf. 734], increases with elevation of the temperature, so that the difference in the thermal conductivity of austenitic and pearlitic steels is smoothed out to a greater or lesser extent at the service temperatures.

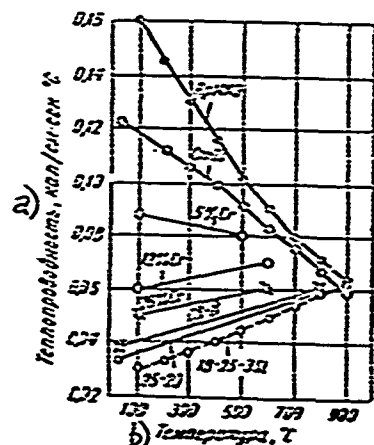


Figure 336. Change in thermal conductivity of various steels with temperature.

(a) Thermal conductivity, cal/cm-sec-°C; (b) Temperature, °C.

High-nickel austenitic steels have a low stability in media containing sulfur dioxides, particularly in the form of hydrogen sulfide. This shortcoming is not inherent in austenitic steels as a whole, but is rather a specific feature of nickel austenite, this apparently being explained, as already pointed out, by the formation of a low melting eutectic. Steels with

a chromium-manganese austenitic matrix are free of this defect.

Protracted heating in the 550 to 500° range, and sometimes even higher, of austenitic steels quenched from a high temperature leads to precipitation of various phases from the solid solution, and this may cause a sharp drop in the plasticity and impact ductility of the steel, accompanied by intercrystalline fracture, particularly if the arrangement of these phases along the grain boundaries is unfavorable. Such phases may also greatly lower the heatproof characteristics. Heating in the stressed state, such as occurs in the process of service of the steel, and work hardening accelerate these processes.

In steel containing no additional elements, the development of brittleness upon protracted heating may be due to the precipitation of the $(Cr, Fe)_{23}C_6$ chromium carbides. In steels containing other carbide-forming elements, such an effect may give rise either to the carbides of the corresponding elements or to a chromium carbide of the $M_{23}C_6$ type in which other elements are dissolved. Thus, for example in the Kh14N14V2X steel this carbide is of the composition $(Cr, Fe, V, Mo)_{23}C_6$ [858]. The danger of occurrence of brittleness of this type increases with increase in the carbon content of the steel, this being illustrated in Figure 557 [824] by the change in impact ductility with change in the length of the heating period at 650° in a steel of the 18-8 with different percentages of carbon. Increase in the amount of carbides in the outer layer due to absorption by them of the carbon in the event of prolonged heating of the steel at temperatures above 700° in a carburizing medium may also lead to drop in plasticity and ductility. The drop in the impact ductility of Kh14N14V2X steel in notched and unnotched specimens versus the depth of cementer layer is shown as an example in Figure 558 [856]. After case-hardening, the specimens were quenched from 1100° and then tempered at 700° for 5 hours for the purpose of precipitation of the carbides from the solution. Chromium-nickel austenitic steels containing no other elements, for example the Kh15N9 and Kh23N13, are only slightly carburized. Of the

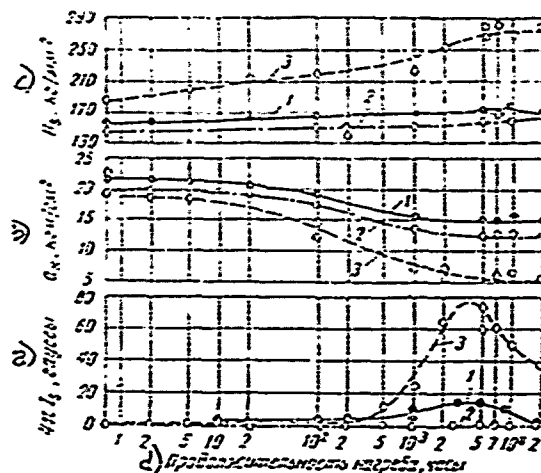


Figure 537. Change in hardness, impact ductility, and magnetic saturation as a result of prolonged heating at 650° in a steel of the 18-8 type with different percentages of carbon:

- 1 - steel with 0.06% C; 2 - steel with 0.07% C;
3 - steel with 0.21% C:

(a) H_s , gauss; (b) a_k , kg/cm^2 ; (c) H_s , kg/cm^2 ;

(d) length of heating period, hours.

additional alloying elements, molybdenum causes the greatest increase in the tendency toward surface carburization; titanium has a fainter effect, and niobium an even fainter one. Additional alloying with silicon greatly reduces the tendency toward carburization [cf. 41].

Carbonitride phases as well are precipitated in steel containing an increased amount of nitrogen when it is heated above 550° , this leading to an additional increase in brittleness. Figure 539 [825] shows as an example the drop in impact ductility versus heating temperature after quenching from 1200° of the 16-25-6 chromium-nickel-molybdenum steel with no nitrogen and with $\sim 0.15\%$ N. A carbonitride phase is precipitated in this steel which at a temperature below 700° and after brief holding (5 hours) at 700 to 800° has the composition $(\text{Cr, Fe, Mo, Ni})_{23}(\text{C, N})_6$, and which after protracted holding at 700 to 900° is converted to the more complex phase $(\text{Fe, Ni})_2(\text{Mo, Cr})_4(\text{C, N})$ [859]. According to the data of [825], the metallic compound Fe_2Mo and a

phase conditionally designated as γ_1 which has a lattice spacing near that of austenite and which may contain about 10% Mo, 14% Cr, 20% Ni, and 35% Fe in solution, are precipitated in the 16-25-6 steel with nitrogen, besides the carbonitride phase, depending on the temperature and length of the heating period. The binary carbide Fe_2Mo_3 and the chromium carbide Cr_{23}C_6 are precipitated in the same steel without nitrogen, besides the γ_1 and Fe_2Mo_3 phases. It is to be seen from Figure 339 that the process of precipitation of the carbonitride phase is accelerated with elevation of the heating temperature to 750 to 800° (Fig. 339a). This is also true of precipitation of carbides (steel with no nitrogen). A comparison of a and b of Figure 339 shows that in the event of a greater length of the heating period the impact ductility drops sharply even at a lower temperature, but the effect of nitrogen diminishes, this apparently being explained both by the quantity and the composition of the phases precipitated.

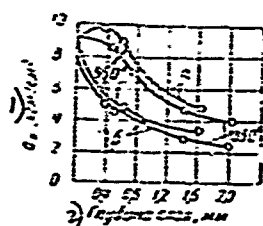


Figure 338. Drop in impact ductility of Kh14N14V2M steel versus depth of case-hardened layer:

a - unnotched specimens; b - notched specimens;
(1) a_k , kg/cm²; (2) depth of layer, mm.

If the austenitic steel is alloyed with additional elements, brittleness may also develop upon prolonged heating as a result of precipitation of metallic compounds from the solid solution. An example is given in Table 92 [823], which pertains to a steel having a relatively stable austenite matrix. In steels 6-9, increase in the niobium content above the quantity required for binding the carbon in the carbides (an Nb:C ratio of up to 40) leads to a sharp drop in impact ductility in the quenched state as well, this being explained by incomplete solution of the niobium carbides and the Fe_3Nb_2 compound at the quenching temperature. The heating of quenched steels at 700° additionally reduces the impact ductility through precipitation of the niobium

carbides and the Fe_3Nb_2 from solution. It is important to note here that the impact ductility drops not only at room temperature, but also at 700° , i.e., at the possible service temperature, although it is slighter than at 20° . Precipitation of the Fe_3Nb_2 phase causes an appreciable deterioration of the heatproof qualities, this apparently being explained by the great tendency of this phase to coagulation. If the steel contains titanium in an amount exceeding that required for binding the carbon, the impact ductility of the steel drops sharply after prolonged heating due to precipitation of the Fe_3Ti phase [824].

The alpha phase, the presence of which in the structure causes a particularly great lowering of the heatproof characteristics of the steel, may be formed in a steel with an insufficiently stable austenitic structure in the event of prolonged heating above 550° (cf. Fig. 312). Precipitation of chromium carbides facilitates formation of the alpha phase in such steel. In fact, it is to be seen from the diagram of Figure 333 that there is a decrease in

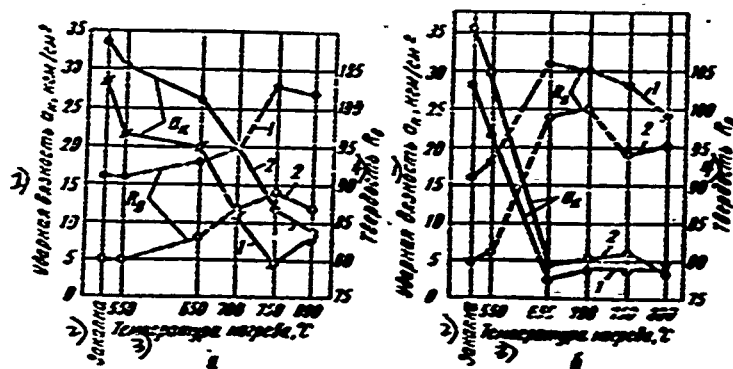


Figure 339. Effect of heating after quenching from 1200° on change in impact ductility and hardness of 16-25-6 steel with no nitrogen (2) and with $\sim 0.15\%$ nitrogen (1): a - heating period of 5 hours; b - heating period of 100 hours; (1) impact ductility a_k , kg/cm^2 ; (2) quenching; (3) heating temperature, $^\circ\text{C}$; (4) hardness, R_B

the stability of the austenite with decrease in the quantity of chromium in

the solid solution, when chromium is present in the amount of 16 to 17%. The precipitation of chromium carbides, on the other hand, leads to impoverishment of the solid solution around them in chromium, this as well facilitating

Table 92

Effect of Molybdenum and Niobium on the Impact Ductility (at Room and High Temperature) of a Steel with a Matrix of 16% Cr and 13% Ni After Quenching from 1100° and After Heating for 1000 Hours at 700°

Number of steel	Chemical composition %			Nb C	σ_k , kg/cm ²		Decrease in σ_k after 1000 hrs at 700°, % of initial value			
	C	Mo	Nb		quenching ¹ from 1100°	1000 hrs at 700° ²				
							Test temperature, °C			
							20	700	20	700
1	0.07	—	0.35	12.1	24.5	24.0	14.7	23.5	40.0	2.0
2	0.07	1.1	0.81	11.6	23.0	23.9	15.0	23.5	34.8	1.4
3	0.07	1.5	0.85	12.1	21.8	29.2	12.9	18.8	40.8	35.6
4	0.05	2.0	0.58	11.6	22.3	27.4	10.2	19.3	54.3	29.5
5	0.07	2.7	0.90	12.9	23.8	26.0	6.4	11.9	73.1	54.2
6	0.04	2.6	—	—	38.1	24.9	11.2	15.7	70.6	37.0
7	0.07	2.7	0.90	12.9	23.8	26.0	6.4	11.9	73.1	54.2
8	0.07	2.4	1.39	19.9	17.2	16.2	7.0	10.6	59.3	34.6
9	0.06	2.4	2.43	40.5	9.6	9.5	4.0	6.4	58.4	32.6

¹Holding for 30 minutes, cooling in water.

²Cooling in air.

formation of the alpha phase. Consequently, the probability of formation of the alpha phase must increase with increase in the steel's content of carbon bound in the chromium carbides. This is confirmed by the variation shown in the lower graph of Figure 337 of magnetic saturation as a function of the length of the heating at 650°, as well as by the change illustrated by Figure 340 [499] in permeability as a function of the intensity field of chromium nickel steel of the 18-8 type with different percentages of carbon. It is to be noted that a certain quantity of the austenite is additionally decomposed under the

action of the thermal stresses arising during cooling in water. The quantity of the alpha phase and the permeability of the steel were somewhat lower in the case of air cooling from the same temperatures.

It may be seen from Figure 340 that after heating at 700° the permeability of the steel varies with changing field intensity as in any ferromagnetic

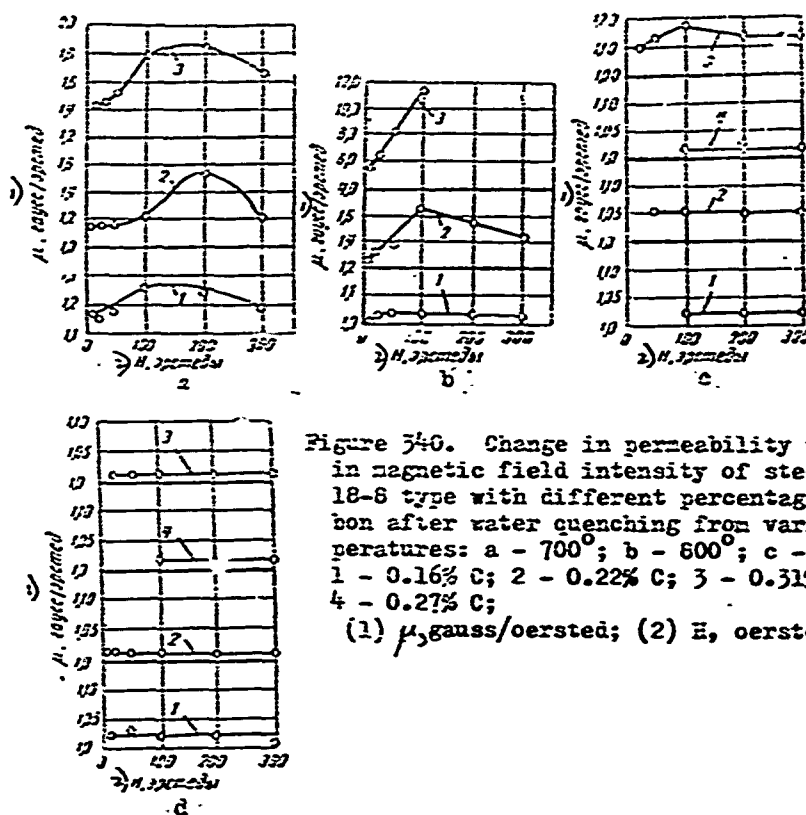


Figure 340. Change in permeability with change in magnetic field intensity of steel of the 18-8 type with different percentages of carbon after water quenching from various temperatures: a - 700° ; b - 800° ; c - 850° ; d - 900° . 1 - 0.16% C; 2 - 0.22% C; 3 - 0.31% C; 4 - 0.27% C; (1) μ , gauss/oersted; (2) H , oersteds.

phase, while producing a maximum the absolute value of which is the greater the higher is the carbon content of the steel. An even greater quantity of carbides is precipitated at 800° , but their reverse solution also begins to be manifested in this case. Hence after heating at 800° of a steel containing 0.16% C, the permeability is low and depends only slightly on the field strength, but with a content of 0.22% and 0.31% C, the quantity of free carbides is greater and the quantity of carbides which have passed into solution

remains the same, so that the permeability rises sharply both with field intensity and in absolute value. Elevation of the heating temperature to 850° leads to increase in the quantity of carbon passing into solution, so that the effect of free carbides is manifested only in the steel containing 0.31%C. Finally, in the event of heating of the steel at 900° , the concentration of the basic mass obtained through reverse solution of the carbides is fully sufficient to compensate for the effect of the free carbides, even if the steel contains 0.31% C, in consequence of which no alpha phase is obtained and the permeability is low in all cases and does not vary with change in the field intensity.

It may consequently be expected that an element which forms more stable carbides than does chromium will reduce the probability of alpha-phase formation due to precipitation of chromium carbides. This is confirmed by the data of Table 95 [499], from which it may be seen that only in the event of the most unfavorable combination of circumstances, specifically 0.32% C and heating at 800° , does steel containing titanium have higher permeability values. With a smaller carbon content, even after heating at 800° the permeability is very low. It is to be noted that in the event the steel is heated to very high temperatures (1200 to 1300°), carbon will be extracted by the intensely carbide-forming element from the solid solution, whereupon the element will, on the contrary, lower the stability of the austenite and contribute to formation of the alpha phase.

It may be concluded from comparison of the curves of change in the magnetic saturation and impact ductility of steels 1 and 2 in Figure 337 that formation of the alpha phase has practically no effect on the impact ductility. It is possible that in the case in question this is explained by the relatively favorable shape and distribution of the alpha phase particles. At any rate, precipitation of the alpha phase is more dangerous to the heatproof characteristics than to the plasticity and ductility of the steel.

Table 92

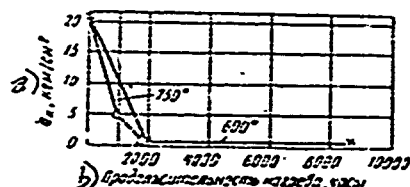
Permeability of Steel of the 18-8 Type with Different Percentages of Carbon and Titanium After Heating at 800 and 850° and Cooling in Water

Chemical composition, %				Permeability μ , gauss/oersted, at a field strength H , oersteds, of					
C	Cr	Ni	Ti	10	25	50	100	200	300
Heating at 800°									
0.18	18.00	8.34	0.23	1.03	1.06	1.09	1.11	1.10	1.09
0.23	18.66	8.28	0.50	1.04	1.04	1.04	1.05	1.06	1.07
0.32	18.17	8.39	0.91	1.16	1.22	1.23	1.31	1.28	1.26
0.31	17.68	8.30	—	5.00	6.80	8.10	11.30	—	—
Heating at 850°									
0.18	18.00	8.34	0.23	—	—	1.01	1.02	1.02	1.02
0.23	18.66	8.28	0.50	1.04	1.05	1.05	1.05	1.05	1.05
0.32	18.17	8.39	0.91	1.06	1.07	1.08	1.09	1.08	1.08
0.31	17.68	8.30	—	—	1.10	1.12	1.16	1.13	1.12

A sharp drop in the impact ductility of the steel after prolonged heating above 550 to 600° may be caused by formation of the sigma phase. Figure 341 [736] shows by way of example, the change in the impact ductility at 20° of the Kh23Kh15 steel versus the length of its heating period at 600 and 750°, a change due chiefly to the tendency of this steel toward formation of the sigma phase; the inadequate stability of the gamma phase also contributes to formation of the sigma phase. The effect of molybdenum on the impact ductility of chromium-nickel steel of the 16-15 type, shown in Table 92, may serve as another example. The sharp drop in the impact ductility of steels 1-5 after heating for 1000 hours at 700° is explained chiefly by the fact that molybdenum contributes to formation of the sigma phase. It is also to be seen from the table that the sharpest drop in impact ductility under the influence of the sigma phase occurs at room temperature. But impact ductility increases greatly even directly at 700°, though to a lesser extent than at 20°. This fact was established long ago in a study by G. V. Estulin [357]. Since the sigma phase plays an important part in thermally stable and heatproof steels, we

shall discuss it in greater detail.

Figure 341. Change in impact ductility at 20° of Kh23M13 steel as a result of prolonged heating at 600 and 750°. (a) α_2 , kg/cm²; (b) heating time, hours.



It was established as early as 1927-1931 [749], that in the event of protracted heating in the 500 to 800° range, a hard, brittle, and nonmagnetic phase is formed in ferrous alloys with 45 to 47% Cr which disappears again upon heating above 950°. This phase has since been detected by numerous investigators under various names (B phase, eta phase, sigma phase, FeCr compound); the designation "sigma phase" being adopted at the present time. The

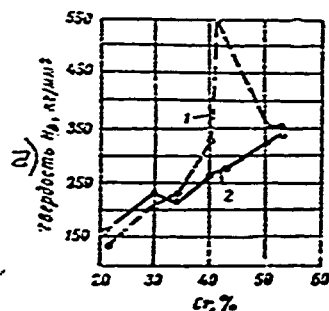


Figure 342. Change in hardness of chromium steels versus chromium content after quenching and annealing (sigma phase formation): 1 - annealing at 820°; 2 - quenching from 1100°. a) Hardness, H_v , kg/mm².

same designation is borne by similar phases which exist in other binary systems (Fe-V, Co-Cr, Co-V, Ni-V) and in many ternary ones. The physical nature and the crystalline structure of the sigma phase have not yet been precisely established. There are experimental data [576] which permit the assumption that the sigma phase has a tetragonal lattice, but the lattice parameters and the ratio of the axes have not yet been determined. According to other data, the sigma phase lattice has the following parameters: $a = 8.66$; $b = 6.21$; $c = 5.18$ Å. On the basis of physical studies of a ferrous alloy with 52.4% Cr, the hypothesis has been advanced [746] that the reconstruction of the crystal lattice and the change in properties upon the transformation $\alpha \rightarrow \sigma$ are the result of electron transition from the chromium to the 3d band of the iron

upon interaction of the atoms of these elements. There are also hypotheses [857] to the effect that the sigma phases represent a compound of the electron type, i. e., their formation is regulated by an electron concentration, which in the case in question equals approximately 7. The shape and position of the sigma phase temperature curve on sections of the ternary Fe-Ni-Cr system lead to the conclusion [747] that this is a phase of the "bertollid" type.

Formation of the sigma phase is accompanied by the liberation of heat, increase in the volume, and a sharp rise in the hardness of the steel. The latter may be seen from Figure 342 [474]. A hardness value of around 1100 kg/mm² has been found in the sigma phase itself in ternary Fe-Cr-Ni alloys [747]. Formation of the sigma phase is also accompanied by a sharp rise in electric resistance, as is to be seen from Figure 343 [474]. The Curie point of binary and ternary sigma phases is located at very low temperatures, and at room temperature they are nonferromagnetic. Thus, the Curie point of the sigma phase of a ferrous alloy with 46.4% Cr is -110°¹.

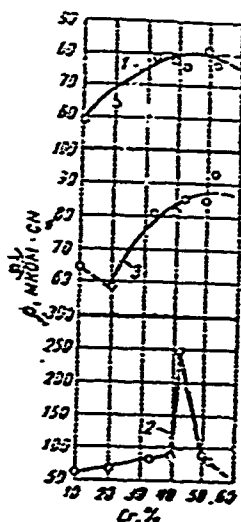


Figure 343. Change in resistivity of chromium steels versus chromium content after different types of heat treatment:
1 - annealing at 980°; 2 - annealing at 820°; 3 - quenching from 1100°;
(ρ) ρ, microhm-cm.

The appearance of the sigma phase, as already pointed out, lowers the plasticity, and particularly the impact ductility of steel, the extent of this

¹M. V. Nevitt and P. A. Beck. J. of Metals, v. 7, 1955, No. 5, pt. 2, p.669

lowering depending on the quantity of the sigma phase, the size of its particles, and their location. Just as any brittle phase, it brings about the greatest brittleness of steel if it is located along the grain boundaries. The plasticity at a high temperature is usually not lowered in this case. The long-term strength is appreciably lowered only by coarse sigma phase particles [583]. The creep resistance of the steel in the case of brief load application even rises somewhat under the influence of the sigma phase, but drops in the event of protracted action of a load [cf. 748, 362]. Thus, the presence of the sigma phase is especially undesirable and dangerous in heat-proof steels intended for lengthy service.

Studies of recent years have shown that formation of the sigma phase occurs through the origination of nucleation centers and their subsequent growth. The function of nucleation centers is apparently played by highly-dispersed particles of an intermediate δ phase, upon whose appearance the impact ductility also drops substantially [583]. Hence, in conformity with the general laws of phase transformations, the kinetic curve of sigma phase formation is also C-shaped. As may be seen from the example shown in Figure 344, [582], with increase in the chromium content in binary alloys from 24 to 33% the value of the minimum which characterizes the duration of the incubation period decreases, and its position is shifted toward the higher temperatures in conformity with displacement of the equilibrium temperature T_0 . It follows that the greater the length of the heating period, the smaller is the chromium content of the steel at which a certain quantity of the sigma phase may be formed.

Many investigators have found that the minimum quantity of chromium in steel at which the sigma phase may be formed, the kinetics of its formation, the value of the equilibrium temperature T_0 depend on the impurities and carbon the steel contains, the presence in it of additional alloying elements, preliminary plastic deformation, and the conditions of manufacture and treatment of the steel.

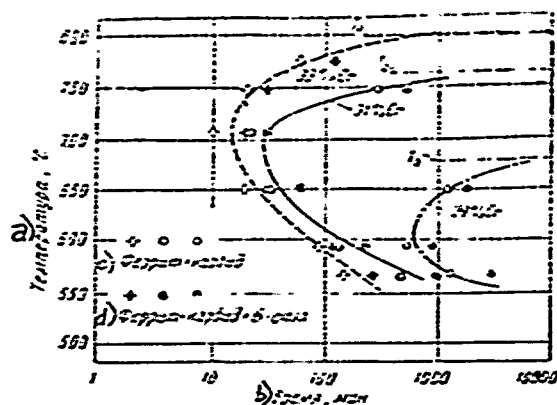


Figure 344. Kinetic curve of sigma phase formation in steel with different percentages of chromium.

(a) temperature, °C; (b) time, min.; (c) ferrite plus carbide; (d) ferrite plus carbide plus sigma phase.

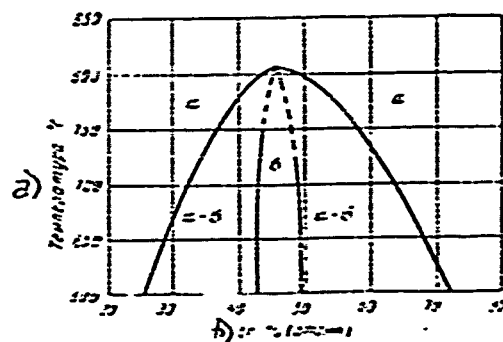


Figure 345. Regions of existence of the sigma phase in a Fe-Cr system in the case of very pure alloys and prolonged exposure of the latter to temperatures below 800°C.

(a) temperature, °C; (b) Cr, % (atomic).

For very pure ferrochromium alloys annealed at temperatures below 800°C for a few weeks, Figure 345 [750] shows a section of the structural diagram, from which it is to be seen that the sigma phase may appear even with a content of > 2% Cr. For relatively pure ternary iron-chromium-nickel alloys annealed for 600 hours, Figure 346a shows the distribution, recently [747] rendered more precise in the δ and $\gamma + \delta$ section, of the phase regions, and Figure 346b illustrates the regions of existence of the sigma phase and of its

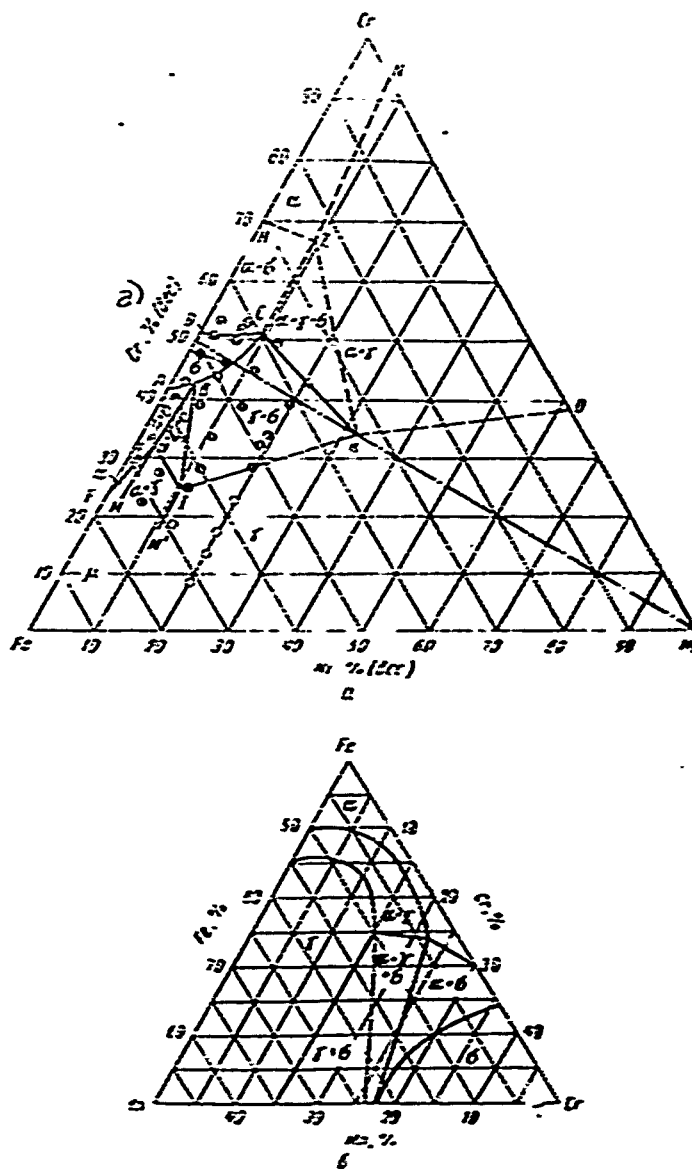


Figure 346. Distribution of phase regions in ternary systems:
 a - Fe-Cr-Ni at room temperature; b - Fe-Cr-Ni at 650°.
 (1) Cr, % (weight).

coexistence with the gamma and alpha phases at 650° for ternary iron-chromium-manganese alloys. However, the effect of the factors referred to, which are not taken into account in plotting of the phase diagram, is that the sigma phase is formed in steels in which it could not be expected on the basis of the structural diagram, including steels of great industrial importance.

It is to be seen from Figure 347 [581] that in the event of preliminary plastic deformation with 95% reduction, the sigma phase is obtained in binary ferrochromium alloys even with a content of 16 to 13% Cr, the equilibrium temperature of its formation, and accordingly that of dissociation, ranging in such alloys from 475 to 650° . The accelerating action of work hardening may also explain the effect of certain other factors on formation of the sigma phase. Thus, for example, [582], the termination of rolling at a reduced temperature accelerates, and the annealing of rolled blanks retards, the formation of the sigma phase. The sigma phase is formed much more easily in rolled blanks than in castings of the same steel at the same heating temperature.

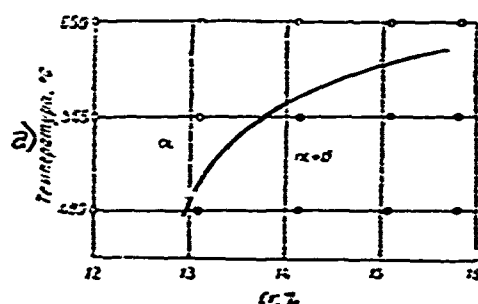


Figure 347. Portion of structural diagram of Fe-Cr alloys with 0.08% C; predeformed by cold working with 95% reduction: o - no sigma phase; • - sigma phase present.
(a) temperature, $^{\circ}\text{C}$.

The impurities contained in commercially pure alloys greatly accelerate the process of formation of the sigma phase (see [Russian] p. 277). Phosphorus has the greatest effect in this respect. The effect of carbon is weaker than that of the impurities, probably because it can exert its effect in opposite directions. Thus, the precipitation of fine carbides accelerates

formation of the sigma phase [582]. Carbon, on the other hand, contributes to formation of the gamma phase and reduces the "effective" chromium content, this impeding formation of the sigma phase. Hence, the effect of carbon, in contrast to that of the impurities, may not be a regular one.

The majority of the additional alloying elements introduced into heat-resistant steels shift the region of existence of the sigma phase toward the lower chromium percentages and lower temperatures, and accelerates its formation [cf. 582 et al.]. A considerable accelerating effect is exerted, for example, by silicon (Fig. 548), aluminum, vanadium, titanium, niobium, molybdenum, and tungsten. Cobalt and nitrogen have a slight effect. Certain of the elements referred to, particularly molybdenum and tungsten, exert a more complex influence. As already noted on p. 278, these elements shift the minimum on the kinetic curve of formation of the sigma phase toward the higher temperatures, and with a content exceeding a certain percentage (over ~5% Mo in Fe-Cr alloys and 2 to 3% Mo in Fe-Cr-Ni alloys), they form the kappa phase, to the kinetics and temperature conditions of whose formation insufficient study has as yet been devoted. It has been established, however [cf. 586], that it is similar in its properties to the sigma phase and that its amount also increases with longer exposure to heating; while plastic deformation accelerates its formation. A new phase, K, nonmagnetic and just as brittle as the sigma phase, which presumably represents a compound of iron with titanium and molybdenum, has been discovered [561] in chromium-nickel steels of the 18-8 type alloyed simultaneously with molybdenum and titanium.

The basic method of reducing the danger of formation of the sigma phase is selection of the proportion of alloying elements which ensures for the steel a stable austenitic structure and the absence of the alpha phase from it. Thus, for example, the formation of sigma phase is scarcely probable in steels containing 14 to 16% Cr and 25 to 30% Ni. Steels of the Kh23X15 and Kh25X18 type, on the other hand, are located so near the boundary of the gamma

and gamma + sigma region on the phase diagram (Fig. 346) that the factors discussed above can easily transfer them to the gamma + sigma region. With the Kh23N13 steel, this may occur even as a result of fluctuations of the chromium and nickel content within the limits of the said brand of steel.

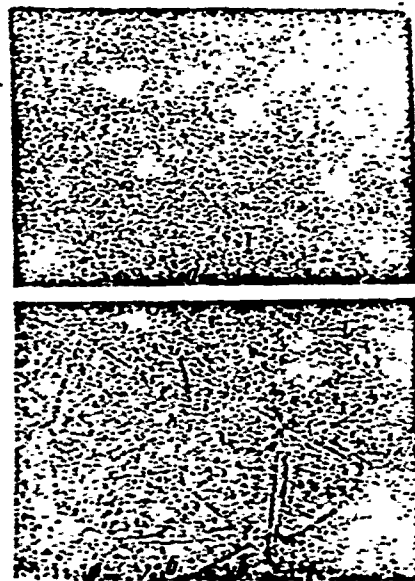


Figure 348. Microstructure of two austenitic steels:
a - 0.08% C, 0.85% Mn, 3.05% Si, 15.72% Ni, 1.53% Al, 17.0% Cr, 0.6% Ti. X 500; b - 0.08% C, 0.76% Mn, 0.52% Si, 15.75% Cr, 17.29% Ni, 2.12% Al, 0.58% Ti. X 300. The arrows indicate the imprints upon measurement of the microhardness.

However, this method does not completely prevent the possibility of obtaining the sigma phase. It has been found in many studies [362 et al.] that the sigma phase may be formed not only as a result of the $\alpha \rightarrow \delta$ or $\gamma \rightarrow \alpha \rightarrow \delta$ transformation, but also directly from the gamma phase, although it is formed more slowly from the latter than from the alpha phase. In addition, prolonged heating may lead to the formation of a certain quantity of the alpha phase even in a steel with a stable austenitic structure [cf. 362 et al.].

We shall point out in conclusion that the $\alpha \rightarrow \delta$ transformation is reversible. Consequently, a steel in which the sigma phase has formed may be corrected by heating to a temperature above 820° (binary Fe-Cr alloys) or above 950° (ternary Fe-Cr-Ni and Fe-Cr-Mn alloys) with subsequent accelerated cooling.

A serious defect of many austenitic heat-resistant (and stainless) steels,

particularly multi-alloyed ones, is their poor deformability in the hot state [cf. 772] (see also [Russian] p. 651). It has become possible in recent years greatly to improve the deformability of such steels by the addition of small quantities of rare-earth elements or their oxides [772, 775, et al.]. A complex concentrate designated as "mischmetall", the principal component of which is cerium, has been put to the greatest use. In addition to cerium, it contains lanthanum, neodymium, samarium, and certain other elements. A number of experiments permit considering the introduction of rare earth elements as more preferable, particularly in normally alloyed austenitic steels (25-20, etc.), not in the form of metals, but in the form of a mixture of their oxides. The surface of the ingots and blanks is also improved in this case, this being highly important for titanium-alloyed steels of the Kh18N9T type. The rare-earth metals or mixtures of their oxides are introduced into the ladle after final deoxidation of the steel. Their optimum quantity varies from 0.9 to 2 to 2.5 kg/ton of the metal and is established experimentally, since it depends on the composition of the steel. In particular, this quantity decreases with increase in the nickel content of the steel, according to certain data. The nature of the effect of the rare-earth elements has not yet been established, but the practical effect is very substantial and makes it possible to increase the weight of the ingot four- or fivefold, as well as to increase the yield of useful metal in consequence of hot forming. In certain steels, such as the 25-20, they widen the range of forging temperatures, thus reducing the danger of overheating.

There is also a report [862] of the possibilities of improving the heat-resistance quality of austenitic steels by the direct and indirect effect of rare-earth elements. Thus, in a steel of the 25-20 type, introduction of the mischmetall in the amount of about 2 kg/ton increased the 100-hour long-term ultimate strength at 650° by 25%. A chromium-nickel valve steel of the 21-12 type is cited as an example of the indirect use of rare-earth elements. This

steel is the best at the present time for the purpose in question, but for certain engines with a high compression ratio, it still is not sufficiently heat-resistant. Alloying of this steel with nitrogen increases its 500-hour long-term ultimate strength at 755° from 8 to 9 kg/mm^2 , with a simultaneous 25 to 30% increase in the plasticity characteristics at failure, but greatly impairs its deformability. Introduction of the mischmetal, on the other hand, in improving the deformability permits utilization of the improved heat-resistance qualities of this steel.

The possibility has been established in the studies of certain Soviet investigators [774 et al.] of improving the deformability of austenitic steel by 0.3 to 0.5% pro rata addition of calcium, this yielding 0.05 to 0.06% Ca in the metal. The authors ascribe the effect of calcium to the fact that it, being a surface-active element, lowers the surface tension of the molten steel and, up to a certain percentage, refines the primary crystals in the ingot. The addition of calcium also increased the long-term strength somewhat and appreciably reduced the creep rate of the investigated steel, which contained 0.05% C, 16.5% Cr, 25.5% Ni, and 6.5% Mo.

Improvement of the technological properties and the yield of useful metal in hot deformation, as is illustrated by studies in recent years [cf. 838/, is also achieved by melting of the steel in vacuo, and particularly if the pouring is also conducted in vacuo. Since there is also an appreciable improvement in the heat resistant qualities in this case (cf. Fig. 313), melting in vacuo presents interesting perspectives.

EXAMPLES OF HEAT-RESISTANT AUSTENITIC STEELS

As examples of heat-resistant chromium-nickel austenitic steels containing no additional alloying elements, we may cite the standardized brands 1Kh18N9T, 1Kh18N12T, 1Kh18N12B (into each of these titanium or niobium is introduced chiefly for the purpose of eliminating intercrystalline corrosion), Kh23N13, and Kh23N18. The foreign steels 25-12 and 255-20, also very widely used, correspond to the last two brands. When they contain 0.3 to 0.45% C, these steels are employed for cast heat-resistant articles. Steels additionally alloyed with silicon in the amount of 2 to 3% with the aim of increasing their corrosion resistance are represented in the Soviet standard by the brands Kh18N25S2, Kh20N14S2, and Kh25N20S2. Brands similar to certain of these are also employed abroad. Thus, for example, in the USA the steel 314 corresponds to the Kh25N20S2. We may cite as examples of steels additionally alloyed with tungsten, molybdenum, and titanium with the aim of improving the heat proofness, the brands 4Kh14N14V2M, 1Kh14N14V2M, and Kh18N12W2T, although the use of the first two is limited at the present time. Steels additionally alloyed simultaneously with tungsten, molybdenum, titanium, and silicon include, for example, the Kh14N14SV2M brand with 4% Si and the EI125, which contains on the average 0.2% C, 2% Si, 0.6% Mn, 15% Cr, 13% Ni, 2% W, and 1% Ti. The basic properties of these steels have been described in the corresponding literature¹ [734, 736, 912, 761, 440, 498, 414, et al.].

Table 94 lists the principal chromium-nickel austenitic heat-resistant steels employed at the present time in US industry and the values of their long-term strength [442; see also 701, 734, 751]. The same table gives the

¹ For lasting duty, see also the bibliographic reference in the footnote and the text to which it refers on p. 570 and [516].

composition of certain German and English steels [610]. Alloying with titanium alone (steel 14) has the aim of hardening the steel through precipitation of a titanium phase, and of simultaneously effecting a saving of costly alloying elements. Steel of this type, which is also employed domestically (the EI424), represents a postwar modification of the 16-30 steel with 1.9 to 2.2% Ti, which was developed during the war in Germany, where it was used, under the designation "tinidur", chiefly for the vanes of gas turbines of jet aircraft. It is interesting to note that, according to German sources [752] this steel (though containing only 1.52% Ti) in the form of an annular forging weighing 210 kg had a low long-term strength and was found to be unfit for use in a stationary steam turbine built in 1946 for operation at a temperature of 600° and a steam pressure of 160 at. It is to be seen from Figure 349 [610] that, with a higher percentage of titanium and an admixture of aluminum, steel of the "tinidur" type (14 in Table 94), with respect to the long-term strength value at 700° is even superior in the event of a brief service life than steel 10, which is alloyed with cobalt. In the event of lengthy service, its strength drops sharply and proves to be lower than that of the others. With respect to the values of elongation at long-term rupture shown in Figure 349, this steel is also far inferior to the steels comparable to it. A domestically¹ developed steel with a similar percentage of chromium and nickel (15-35), but additionally alloyed with titanium and tungsten (the EI612) has better properties for long-term duty at temperatures up to 650°.

The majority of the steels listed in Table 94 are strengthened by semi-hardening. Steel 9 is strengthened by precipitation hardening through a cuprous phase, steel 4 through a carbide phase, and steel 8a through an α' phase. Steel 2 or 16-25-6 (domestic steel EI395), capable of being structurally hardened [cf. 580 et al.], may be most effectively strengthened while

¹A. V. Stanyukovich. Metallovedeniye i obrabotka metallov, No. 12, 1957, p.26.

acquiring the best properties at room and high temperatures, through a combination of semi-hardening and precipitation aging, which is apparently intensified by cold working. This is achieved by quenching from a temperature

Table 94

Chemical Composition of Certain Heat-Resistant Complex-Alloyed Chromium-Nickel Austenitic Steels¹ Employed in England, the USA, German Federal Republic and German Democratic Republic.

No. of steel	Designation of steel	Chemical composition (avg.), %											Long-term strength, kg/mm ² , at a temperature, °C, of			
		C	Si	Mn	Ni	Cr	Mo	Nb + Ta	Co	Ti	W	Other	550		615	
													100 hrs	1000 hrs	100 hrs	1000 hrs
1	GT-45	0.12	0.5	0.75	14.1	15.9	2.5	0.45	—	0.25	—	—	30	26	12.0	2.4
2	16-25-6	0.10	0.7	1.35	25.0	16.0	6.0	—	—	—	—	0.15N	32	24	9.5	6.3
3	19-9DL	0.30	0.6	1.10	9.0	19.0	1.25	0.40	—	0.30	1.2	—	37	27	12.0	7.0
4	N-155	0.15	0.5	1.50	20.0	21.0	3.0	1.00	20.0	—	2.5	0.15N	35	28	8.4	5.6
5	IME	0.10	0.7	0.50	12.4	19.0	—	1.20	—	—	3.2	0.15N	31	25	—	—
6	CSA	0.25	0.4	5.00	5.0	18.0	—	1.00	—	—	1.3	—	35	27	—	—
7	HS-68	0.07	0.5	1.50	15.0	12.5	2.0	—	—	0.60	0.60	0.025B	41	34	18.0	11.0
8	Refract alloy 3	0.07	—	—	30.0	25.0	3.0	—	—	—	—	—	—	—	—	—
8a	A-235	0.05	0.95	1.35	25.0	15.0	1.75	—	—	2.0	—	0.2Al + 0.3V	43	32	9.7	5.4
9	—	0.2%	—	—	17	17	3	—	7	0.8	—	3 Cu	—	—	—	—
10	G18(S)	0.40	—	—	13	13	2	3	10	—	2.5	—	—	—	—	—
11	—	0.05	—	—	16	16	2	0.8	—	—	—	—	—	—	—	—
12	—	0.08	—	—	16	16	2	0.8	—	—	—	0.05B	—	—	—	—
13	—	0.08	—	—	13	16	1.5	0.8	—	—	—	0.7V + 0.15N	—	—	—	—
14	—	0.10	—	—	30	15	—	—	—	1.7	—	Al	—	—	—	—

¹ Steels 1-8 are used in the USA; 9 and 10 in England; 11-14 in Germany (steels 12 and 13 were introduced after the war).

² Fe -- remainder.

of around 1175°, followed by deformation with 20 to 30% reduction at a temperature of 650 to 750°, which is below the recrystallization temperature of the given steel (980 to 1040°), and tempering at a temperature of around 700°. The

recently published results [753] of studies not yet completed show that in this steel 10% of the nickel may be replaced by 6% manganese without detrimentally affecting its properties. In the Soviet Union the 16-25-6 steel (EI395) is being supplanted by a steel with a chromium-manganese-nickel austenitic matrix, containing on the average 0.57% C, 12.5% Cr, 8.5% Mn, 3% Ni, 1.25% Mo, 1.4% V, and 0.6% Nb (the EI481 steel) and used for parts with a short service life. A steel of approximately the same composition as steel 5 is also used domestically (the EI572 steel). As may be seen from Table 94, it has a high long-term strength, this being the result, as with a number of other steels, of alloying with a relatively small quantity of tungsten and niobium. It also possesses a high relaxation resistance and low notch sensitivity, but its structure must not contain more than 5% ferrite in the form of fine zones within the austenite grains¹.

Table 94 gives only the long-term strength values for 100 and 1000 hour periods. There are as yet no sufficient data on the properties of these steels with respect to long-service life. Of interest are, therefore, the data given in the German report referred to above [752] on the behavior after 50,000 hours of certain austenitic steels from which responsible turbine parts were manufactured to operate at a temperature of 600° and steam pressure of 160 atm. A disk 850 mm in diameter, 180 mm in thickness, and weighing 614 kg, which was subjected to work hardening with 10% reduction at a temperature below the recrystallization point, was forged from a steel (AT SW) containing 0.08% C, 0.6% Si, 1.1% Mn, 16% Cr, 13% Ni, 2% Mo, 1% Nb + Ta, and 0.15% N, i.e., steel 15 in Table 94, but containing no vanadium. In specimens of this forging -- which is currently in service -- the long-term strength obtained by extrapolation to 100,000 hours is 15 kg/mm², while it is only 9 kg/mm² in the same steel but in quenched state without cold work. The effect of work

¹A. V. Stanyukovich. Metallovedeniye i obrabotka metallov, No. 12, 1957, p. 26.

hardening was retained after 30,000 hours of service at 600°. It is interesting to note that this steel essentially is a modification of the steel 16-13-5 used earlier in the USA (prior to introduction of the steel 16-25-6), which in place of 1% Mo contains the same amount of niobium and 0.15% N.

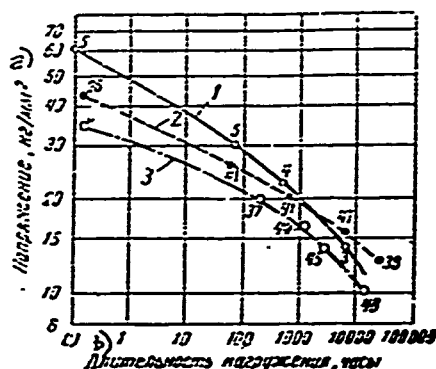


Figure 349. Breaking stress versus duration of load application at 700° in "tinidur" steel as compared to other steels:

1 - steel 14 (tinidur) with 0.15% C, 15% Cr, 30% Ni, 1.7% Ti, + Al; 2 - steel 10 with 0.4% C, 13% Cr, 13% Ni, 2% Mo, 2.5% W, 3% Nb, 10% Co; 3 - steel 12 with 0.08% C, 16% Cr, 16% Ni, 2% Mo, 0.6% Nb, 0.05% B. The numbers by the points designate the values of δ , %, at failure ($i = 5\delta$). (a) stress, kg/mm²; (b) duration of load application, hours.

A steel with 0.06% C, 0.9% Si, 1.3% Mn, 16% Cr, 22% Ni, 1.4% Mo, 0.9% Nb + Ta, and 0.15% N has proved itself valuable for parts which must not be subjected to cold working or which require welding. With respect to the long-term strength after 30,000 hours, it is superior without cold work to the preceding brand (the steel AT SW) in the work hardened state. Steels 12 and 13 of Table 94 were introduced in the Federal Republic of Germany after the war as relatively economical brands precisely for the parts of stationary installations designed to operate at temperatures up to 650°. In steel 12 the nickel content has been increased to 16% with the aim of producing more stable austenite. This goal is reached in steel 13 by the introduction of nitrogen. To

increase the stability of the austenite, the nickel content was also increased to 16% in steel 11 (Table 94). This is a prewar modification of the steel 16-13-3 in which 1% Mo has been replaced by 0.8% Nb. A similar 16-13 steel with 2% Mo and 1% Nb is also used domestically (the EI405).

Austenitic steels additionally alloyed with cobalt stand up well at temperatures up to 600 to 650°. An example is steel 10 (Table 94) used in England. A modification of this steel with a somewhat higher tungsten and molybdenum content, reduced content of niobium and with vanadium and titanium additionally introduced in small quantities is also employed domestically (the EI434). Steels of a similar type have been developed domestically [869] and used for the manufacture of cast parts of powerful steam turbines designed for operation at temperatures above 550° and under high pressure for 100,000 hours.

An idea of heatproofness of steel 4 (Table 94), which contains even more cobalt, in long-term service may be gained from the recently published results [849] of tests of this type of steel conducted for periods attaining 10,000 to 12,000 hours. It may be seen from Figure 350 that the value of the long-term ultimate strength at 660° and duration of 20,000 hours obtained by extrapolation is 18 kg/cm², and 16 kg/cm² for a duration of 100,000 hours. The alloy resists relaxation fairly well at the same temperature for a period of 12,000 hours. With a continuous application of load during approximately 10,000 hours, ultimate elongation did not fall below 14%. The impact ductility at 20° after isothermal holding at 660 and 700° for 2000 to 5000 hours drops from 8 to 2 kg/cm², but subsequently remains constant for about 10,000 hours. The hardness varies little upon isothermal holding. No precipitation of a ferromagnetic phase is detected. The authors ascribe the relatively high stability of the structure and properties of the alloy principally to the effect of cobalt. The precipitated phases consist of NbC and M₂₃C₆ carbides, their chromium content remaining constant for 10,000 hours at 660°, but the molybdenum content increasing from 9 to 15% and that of tungsten from 7 to 18.5%. More-

over, a phase has been detected whose composition and structure it has not been possible to define. It is probable that this phase plays an important part in the stability of the alloy, particularly after a 5000-hours of load application.

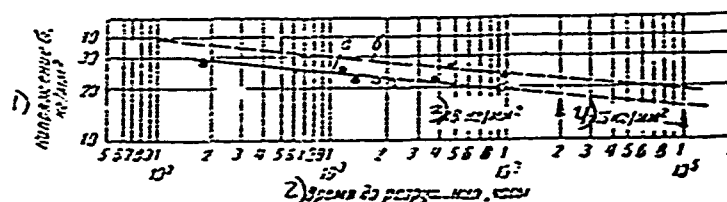


Figure 350. Long-term strength of alloy with $\sim 20\%$ Cr, 20% Ni, and 20% Co at 650° . Oil quenching from 1200° . Tempering: a - smooth specimens: 760° , 70 hours; b - notched specimens: 800° , 45 hours.
(1) stress σ , kg/mm^2 ; (2) time to failure, hours;
(3) 18 kg/mm^2 ; (4) 15 kg/mm^2 .

The results have recently been published of extensive research relative to the long-term service life. This research was conducted in accordance with a single program simultaneously at a number of plants and at research institutes in the German Democratic Republic and the Federal Republic of Germany and certain other countries (USA, France, Czechoslovakia, Sweden, Switzerland). These investigations involving tests continuing for 50,000 hours at temperatures up to 700° , are being conducted in the German Democratic Republic and the Federal Republic of Germany with 25 ferritic and 12 austenitic steels, as well as with 9 non-ferrous alloys. Unfortunately, we were not in a position to give here the most important data obtained in this research and refer the reader to the original source¹.

C. HEAT-RESISTANT NICKEL AND COBALT-BASED ALLOYS

The urgent need for a further rise of the heat resistance of metals led during the war, and especially during the postwar years, to the development of

¹Archiv Eisenhüttenwesen, Bd. 28, 1957, No. 5/6 (Mai/Juni) and No. 11 (November).

a large number of complex nickel and cobalt based alloys and to their constant improvement. Many of these alloys contain a large quantity of both cobalt and nickel simultaneously, and are, therefore, frequently placed in an independent group of alloys on a nickel-cobalt base. The advantages of alloys of this type (Fig. 95) are to be seen from Figure 351 [810].

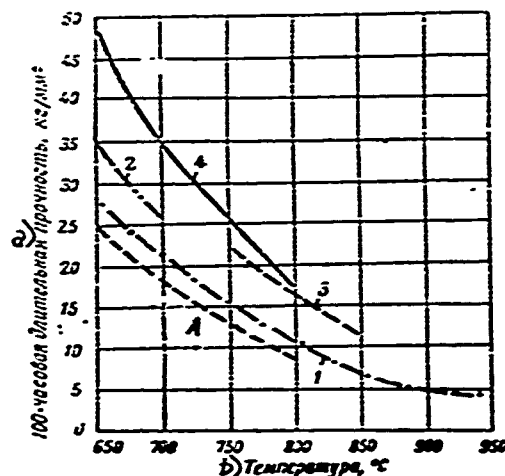


Figure 351. Values of 1000-hour long-term strength at various temperatures for certain nickel-cobalt based alloys (used in Germany) in comparison with steel 10 alloyed with cobalt (curve A; cf. Table 10 for the composition of the steel). The numbers of the curves correspond to the alloys whose composition is given in Table 95.

(a) 1000-hour long-term strength, kg/mm^2 ; (b) temperature, $^{\circ}\text{C}$.

Alloy 1 is the somewhat modified American alloy W-155, classified in Table 94 among the complex-alloyed austenitic steels (steel 4). It is to be seen from Figure 351 that up to 800° alloy 4 (Table 95) is superior to the others. It is principally alloy 3 which is used for turbine vanes.

Table 96 [442, see also 701, 754, 751, 912] gives the alloys based on nickel and cobalt which are employed at the present time in US industry and the values of their long-term strength. Alloys of nickel and chromium or chromium and iron, known under the designations Nichrome and Ferronichrome,

possess a very high corrosion resistance and have long been used as high-resistivity alloys for heater elements, etc. However, their heat resistance is relatively low. Thus, it is to be seen from Figure 352 [47] that the curves of creep strength (stress at which the average creep rate does not exceed 10^{-4} %/hour) versus temperature practically coincide for Ferronichrome 15-60 (60% Ni, 15% Cr, 25% Fe), for Nichrome 20-80, and for austenitic steel 20-25, although the creep strength of the Nichromes may be raised by elevating the

Table 95

Chemical Composition (average, %) of Nickel-Cobalt-Based Alloys
Employed in the German Democratic Republic and the Federal
Republic of Germany

No. of alloy	C	Cr	Ni	Co	Mo	V	Nb	Ti	Other
1	<0.1	15	20	20	2.5	2.0	0.8	—	0.7%V; 0.15%N
2	<0.1	15	35	23	4.5	4.5	—	1.7*	—
3	0.3	19	10	45	2	—	1.5	—	3%V
4	<0.1	20	25	36	—	12	1.5	2.0	0.8%Al

* A variant is used with 5% Ta, which possesses better heatproof qualities.

quenching temperature (the alloys of Fig. 352 were quenched from 1000 to 1675°). As may be seen from Table 96, the 15-76-8 Ferronichrome Inconel (2) also has a low long-term strength. Nickel alloys with 25 to 35% Cr have much better heatproofness, as is to be seen from Figure 310. However, the practical utilization of such alloys is impeded by their poor technological properties. Moreover, as was recently established, prolonged heating of alloys with 20 to 30% Cr, at temperatures below 550° leads to formation of the compound Ni_3Cr [cf. 115], the effect of which on the most important properties of these alloys has not yet been studied. Hence Nichromes without additional alloying are employed where high corrosion resistance is required in addition to average heatproof qualities, such as for flues in aircraft gas turbines.

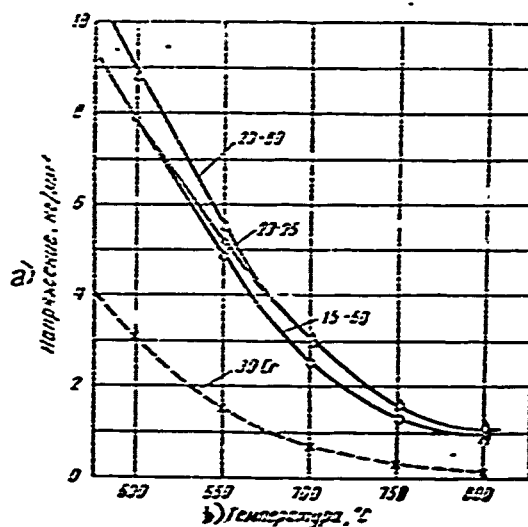


Figure 352. Limited creep stress versus temperature for certain nickel-based alloys and austenitic steels.
(a) stress, kg/mm^2 ; (b) temperature, $^{\circ}\text{C}$.

The basic method of improving the heatproofness of Nichromes consists in alloying with titanium and aluminum in order to render them structurally hardening alloys through the α' phase. As a result of this fact their carbon content is low. Of importance in this process is not so much the strengthening caused by this treatment as the disperse precipitation of the α' phase itself [cf. 442], which (see [Russian] p. 520) has a high interatomic bond strength and resistance to coagulation. Hence annealing of these alloys is usually conducted at a temperature lying beyond the hardness curve maximum, and for a lengthy period. With respect to their heatproofness (cf. Table 96), in addition to titanium and aluminum these alloys are also fused with cobalt and molybdenum which also strengthen the solid solution, and are similar to cobalt-based alloys, or are superior to them, even at a temperature of 870° . Such alloys include, in particular, Nimonic 100 (15 in Table 96).

Further research in this field is thus being conducted with cobalt-free or low-cobalt alloys based on nickel. That such research may yield substantial

results is indicated, for example, by the very high heat resistance of cast nickel alloys with chromium, molybdenum, aluminum, niobium, and boron [174]. The 100-hour long-term strength of alloys of this type containing 12 to 15% Cr, 5 to 6% Mo, 5.5 to 7% Al, 2% Nb, 0.5% B, and 4.5% Fe is 10.5 to 14 kg/mm². Mention is also made in the literature [161] of an alloy (GMR) containing 0.1 to 0.2% C, 14 to 17% Cr, 4.5 to 6.0% Mo, 2.5 to 3.5% Al, 1.5 to 2.5% Ti, and 0.025 to 0.1% B, and a test alloy of similar composition but containing 10% Cr, no molybdenum, and 0.5% Cr. However, the time factor exerts a very strong effect on these alloys, and when the test continues for 1000 hours, their strength manifests a greater drop than in the case of the other alloys. Moreover, they must be brittle at room temperature. One can scarcely doubt the possibility of further improvement and of achieving positive results in utilizing other alloying elements.

The Hastelloys which basically represent nickel alloys with molybdenum and chromium, are also cited among the nickel-based alloys. With respect to their long-term strength (cf. Table 96) and creep resistance, they are inferior to most other nickel-based alloys, and their use is justified by the fact that they possess a high chemical stability in a number of aggressive media. Hence they will be discussed in the chapter on the alloying of stainless and acid-resistant steels. Alloys of this type, but with a higher chromium content, are sometimes employed for parts which in addition to average heatproofness must possess a very high corrosion resistance. We may cite as an example an alloy containing 0.5% C, 1% Mn, 1.2% Si, 26 to 27% Cr, 45 to 50% Ni, 5% W, and the remainder Fe, which was fairly stable in service at temperatures up to 1250° for up to 2500 hours [850].

Cobalt-based alloys usually contain an increased amount of carbon and carbide-forming elements -- molybdenum, tungsten, niobium (cf. Table 96) -- and have high heatproofness due to the very stable carbide phases located in the heatproof matrix. Hence they normally do not require precipitation

hardening¹. Certain of them are employed as cast alloys, while articles are made of them by the method of precision casting. The high resistance of the carbide phases (and possibly that of the metallic compounds CoCr, CoNi, and CoW as well) to coagulation at high temperatures apparently explains the fact that with respect to their heatproofness the cobalt-based alloys (cf. Table 96) are far superior to nickel-based alloys only at 850 to 950°. At lower temperatures, not only do they offer no advantages over the cheaper nickel-based alloys, but are even inferior to them.

Alloy 18 in Table 96, which is known under the name "vitallium", in addition to its high heatproofness possesses a high resistance to corrosion in a number of very aggressive media. Since it has been found to be one of the most stable it was put to wide use in surgery as a material for plates, screws, etc., in bone-knitting operations and the like.

High-carbon cobalt-based alloys of the Stellite type are also employed as heatproofness alloys. Thus, for example, the possibility is reported [754] of employing an alloy with 0.8% C, 20% Cr, 12% Ni, 45% Co, 2% Mo, 1.2% Nb, and 2.6% V for the manufacture of gas turbine rotor vanes by casting method, since a permissible straggling of the properties at 750 to 800° is obtained in this case. The Stellites are also utilized as hard facings to increase the surface hardness of parts of heat-resistant austenitic steels. However, it is not always possible in this case to utilize their highest hardness, since alloys with a lower hardness have greater corrosion resistance [see, for example, 752].

Alloys which have a high damping ratio have recently [446] been found among the cobalt-based ferromagnetic alloys. As may be seen from Figure 326 given earlier, this property is possessed by binary cobalt alloys with 35% Ni or 20% Fe and by a ternary cobalt alloy with 28% Fe and 7% Ni. The Co-Ni alloy

¹It is apparently precisely on the basis of these characteristics that the authors of [442] classify alloy 16 of Table 96 also among the cobalt-based alloys.

Table 2
Chemical composition and long-term strength of heat-resistant nickel and cobalt-based alloys employed in the USA

No. of alloy	Designation of alloy	Chemical composition (avg., %)										Long-term strength, kg/mm ² , at a temperature, °C, of																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																						
		C	Si	Mn	Ni	Co	Fe	Mo	Nb + Ti	Al	W	650					815					870					940																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
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1	Nimonic 75	0.12	0.6	0.4	70	—	20	2.4	—	0.60	0.4	15	10	40	2.0	—	2.05	1.0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

* Chut.

**According to data in Metal Industry, v. 89, 1956, p. 132, and Iron and Steel, v. 28, 1957, p. 42.

has good technological properties and high heatproofness. Having a relatively high Curie point, it can retain the high damping ratio to a temperature of around 650° and in this respect it is basically suitable as a material for the first stage vanes of steam turbines which operate at such temperatures.

It must be noted in conclusion that the fireproofness of a steel or alloy of the same composition may vary widely in relation to the melting conditions. This follows from theoretical considerations, since the melting method may have a great effect on the composition and structure of the boundary layer of the grain. Thus, for example, much higher creep resistance, time to failure, and plasticity characteristics at failure were obtained [810] with a chromium-nickel austenitic steel of the 16-15 and 16-16 type containing niobium, as well as with an alloy of type 1 in Table 95, these being melted in a high-frequency furnace under a vacuum (at a residual pressure lower than 0.1 mm Hg), than with the same alloys melted in an open high-frequency furnace. An example of substantial increase in the long-term strength due to melting in vacuo for a nickel based alloy (alloy 11 in Table 96) was given in Figure 915. Similar results were obtained for alloy 12, Table 96, and others [839].

Melting in vacuo permits obtaining nickel and cobalt-based alloys of high plasticity at high-temperature creep rupture without the use of deoxidation by silicon and manganese. In this case the vacuum melts contain one-eighth to one-tenth as much non-metallic impurities, and impurities of smaller size, as in the conventional alloys. This constitutes an additional contribution towards better deformability of ingots in the hot state. And since nickel and cobalt-based alloys possess poor deformability, this circumstance is of very great importance for them. At the present time, the melting of a number of highly fireproof alloys -- and in certain cases also the pouring -- are done in vacuo on an industrial scale. According to available information [cf. 838], 30 to 40 firms in the USA either are already melting, or will in the near future begin melting, fireproof alloys in vacuo.

D. HEAT-RESISTANT ALLOYS BASED ON HIGH-MELTING METALS AND SPECIAL ALLOYS

Intensive research of alloys based on high-melting metals, as well as of the possibilities of utilizing combinations of metals and ceramic materials, is being conducted in all countries with the aim of finding materials possessed of especially high heat-resistance for brief periods of service. Discussion of such alloys and special materials goes beyond the scope of our subject. Hence we shall limit ourselves to pointing out only the basic trends of this research and the problems arising in it.

Since the melting point in the first rough approximation characterizes the interatomic bond strength, it is natural to expect that alloys based on high-melting metals should possess especially high heat-resistance. However, not all high-melting metals and their alloys are highly heat-resistant. Some idea of the relative fitness of such metals as matrices for heat resistant alloys may be gained from Table 97 [155]. The stress σ causing a deformation of 1% in 24 hours is adopted here as the criterion of the relative creep resistance. The ratio of the value of σ to the specific gravity is an important characteristic for such articles as turbine vanes, in which a considerable portion of the arising stresses is caused by forces of inertia. These stresses, other conditions being equal, are, therefore, proportional to the specific gravity of the material. Consequently, with identical values of the stress which causes a desired deformation under identical service conditions, the better material will be the one with the lower specific gravity, since the stress in it will be lower. It may be seen from Table 97 that in nickel, and particularly in iron and cobalt, a desired deformation is achieved under these test conditions with a higher stress than in other metals with higher melting points. The most suitable to serve as possible matrices for alloys with high heat-resistance are chromium, molybdenum, tungsten, tantalum, niobium, rhodium, and iridium.

Table 62

Relative creep resistance of certain metals. Compression creep testing at 10000 in vacuum.

	Ti	Zr	V	Nb	Ta	Cr	Al	W	Pt	Pd	Rh	Ir	Fe	Co	Ni
σ , kg/mm ²	~0.16	~0.16	0.46	4.34	4.65-- 6.20	3.10-- 4.65	4.65-- 6.20	9.3	~0.16	0.46	4.60	9.30	0.74	0.96	0.69
specific gravity ρ , g/cm ³	4.5	0.5	0.1	8.4	16.0	7.1	10.4	19.3	21.4	11.9	12.4	22.4	7.87	8.9	8.9
σ/ρ ratio (for 10000)	0.013	0.0323	0.076	0.52	0.28-- 0.37	0.44-- 0.65	0.45-- 0.60	0.48	0.007	0.039	0.37	0.41	0.091	0.11	0.077

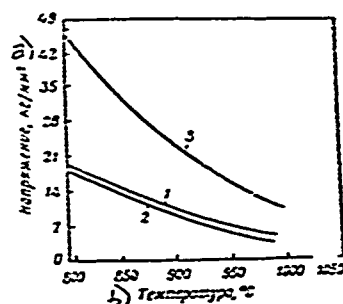


Figure 353. Values of 100-hour long-term ultimate strength at high temperatures of an alloy of Ti + 36% Al in comparison with a cobalt-based alloy:

1 - alloy of Ti + 36% Al; 2 - S-816 alloy (17 in Table 96); 3 - alloy of Ti + 36% Al with allowance made for its specific gravity;

(a) stress, kg/mm^2 ; (b) Temperature, $^{\circ}\text{C}$.

As follows from Table 97, titanium is little suited for this purpose. However, a recently investigated alloy of titanium with 36% Al, as may be seen from Figure 353 [914], is superior to the cobalt-based alloy S-816 (alloy 17 in Table 96) at temperatures up to $\sim 1000^{\circ}$ with respect to the 100-hour ultimate strength. The difference is especially great if allowance is made for the low specific gravity of the titanium alloy (curve 3 in Figure 353). This alloy is sufficiently heatproof at 1000° and the introduction of 5 to 7% Nb into it renders it corrosion resistant even at 1200° for ~ 100 hours. The Ti + 36% Al alloy has not yet been put to independent use due to its very low plasticity and ductility at room temperature, and because of the fact that its other important properties have not yet been studied; however, it may serve as a base for research of light highly heat-resistant alloys.

Chromium-based alloys were first studied from this standpoint over 10 years ago [454]. A large number of binary and ternary systems based on chromium have been investigated since that time. The best combinations of strength and plasticity in tests conducted over the 875 to 925° range have thus far been found in alloys containing 60% Cr, 15% Mo, and 25% Fe, or 60% Cr, 25% Mo, and 15% Fe. Upon transition from the first composition to the second, the strength rises and the plasticity drops with increasing molybdenum content and decreasing iron content. In the second alloy, the long-term ultimate strength at 870° is 14 kg/mm^2 with a 9% elongation, in 100 hours. This

renders it approximately equivalent to a cast cobalt-based alloy (19 in Table 96).

The principal problems for chromium alloys consist in the development of efficient methods of melting them and primarily in lowering their critical brittleness point, and, in particular, in obtaining a satisfactory plasticity and impact ductility at room temperature. Considerable success has been achieved in the solution of the first problem [cf. 756]. The causes and methods of lowering the brittleness of chromium and its alloys have also been studied in a number of works [cf. 113, 757, et al.]. Nevertheless, there is still no unified view as to the cause of the brittleness of chromium. Some hold oxygen to be responsible for the brittleness, while others believe it to be nitrogen, which forms a solid solution with chromium. It is most probable that brittleness is intensified by oxygen, as well as by nitrogen, and carbon, but that nitrogen has the greatest effect¹. Hence it is recommended that the melting of chromium alloys be conducted under conditions which prevent or reduce the possibility of their absorbing nitrogen, oxygen and carbon. Many metallic elements in chromium, such as aluminum, copper, nickel, manganese, cobalt, and iron (in the order of diminishing extent of influence) also elevate its critical brittleness point. Even with the purest chromium, obtained by the iodide method, the critical brittleness point is still far above room temperature.

There is still little information in the literature concerning the composition and treatment of alloys based on molybdenum. It is to be seen from the comparison shown in Figure 354 [cf. 751, 810] that with respect to the 1000-hour long-term strength molybdenum alloys are far superior at temperatures of 850 to 1000° to alloys based on cobalt (alloy 6) and may be used in service

¹Cf. R. W. Fountain and M. Korchynsky. Journal of Metals, v. 9, 1957, No. 7, p. 966.

at temperatures up to 1100° . One of the disadvantages of molybdenum, for the reason noted above, is its greater specific gravity than those of nickel and cobalt alloys. This disadvantage is inherent to a much greater extent in tungsten. The derivation of pure molybdenum, as well as the methods of melting and reforming molybdenum alloys, cause no especially serious difficulties. The principal problems for molybdenum and tungsten alloys are due to the fact that they (just as chromium alloys) have a high cold shortness and, chiefly, low resistance to oxidation at temperatures above 600° . Above 750° the oxides of molybdenum are highly volatile and can play no protective role. Insofar as may be judged from technical and patent literature, intensive work is being carried on toward solution of these problems. In particular, search for surface coatings and plating methods has been conducted for a number of years, with the aim of increasing the corrosion resistance of molybdenum. Coating (75μ) consisting of MoS_2 or plating (75μ) with Nichrome (80% Ni + 20% Cr) has thus far been found to be the most effective.

Much success has been achieved in recent years in the development and application of various highly heatproof materials based on carbides, borides, nitrides, silicides, aluminides, and oxides. Hence the following are apparently of the greatest interest: titanium carbides with an admixture of tantalum carbides, niobium or chromium, zirconium carbides, titanium and chromium, molybdenum and titanium silicides, and others. To reduce the brittleness, to increase the resistance to abrupt temperature changes, etc., powders of these materials are mixed with powders of various metals, chiefly nickel, cobalt, chromium, and their alloys, in a definite ratio. Hence they are termed cermets or cermetes. Some information on the methods of manufacture and the properties of the cermets may be found in the literature [750, 754, 755, 759]. The values of the 1000-hour long-term strength at high temperatures are shown in Figure 554 for two cermets based on titanium carbides. Shown in the same figure is the long-term strength at 980° of a cermet based on chromium boride, nickel

aluminide, and a complex matrix consisting of titanium carbides and borides, and silicides. The cermet based on the aluminides, particularly the nickel aluminides, is interesting for the fact that it possesses the lowest brittleness of the cermets, but its long-term strength is still relatively low. Porous cooled materials, for turbine vanes for example, may be classified among the special materials, even if they are manufactured by powder metallurgy methods from conventional alloys. Other special materials are also being developed which are manufactured by the powder metallurgy method and which have a basic mass of metal strengthened by disperse particles¹ such as $\text{Al-Al}_2\text{O}_3(\text{SiP})$, $\text{Cu-Al}_2\text{O}_3$, $\text{Ni-Al}_2\text{O}_3$, Mo-TiO_2 , $\text{Be-Be}_2\text{C}$, etc. Such materials have a much higher ductility than the conventional cermets.

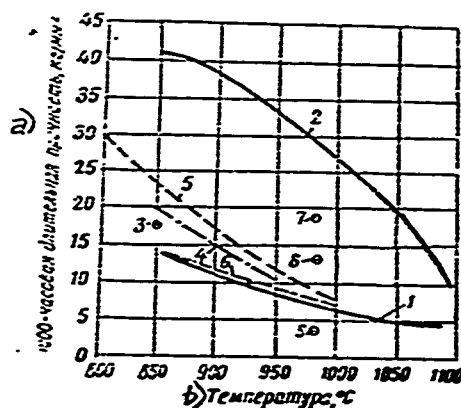


Figure 354. Comparison of values of 1000-hour long-term strength at various temperatures for alloys based on molybdenum, chromium, and cobalt, and for certain cermets:

- 1 - commercially pure Mo; 2 - alloy of Mo with 0.5% Ti; 3 - 60% Cr, 25% Mo, 15% Fe; 4 - 60% TiC + 32% Ni, 8% Cr; 5 - 50% TiC + 30% Ni, 10% Co, 10% Cr; 6 - 0.5% C, 25% Cr, 10% Ni, 55% Co, 8% W; 7 - 55% TiC + 18% TiB₂ + 11% Co, 10% Si; 8 - chromium boride + metal; 9 - nickel aluminide;
- (a) 1000-hour long-term strength, kg/cm²;
- (b) temperature, °C.

¹See, for example, K. J. Grant and O. Preston. Journal of Metals, v. 9, 1957, No. 3, p. 349.

X. ALLOYING OF STAINLESS AND ACID-RESISTANT STEEL

Steels of this type, in addition to corrosion resistance in given media, must also possess various other properties. They are employed the most frequently for the parts of various machines and devices. Hence they must also possess sufficiently high mechanical properties. If such steel is intended for the manufacture of rustproof tools, it must have a high hardness and wear resistance. Stainless and acid-resistant steels are also widely used as thermally stable and heat-resistant steels. They were discussed from this standpoint in the preceding chapter. Finally, it is required that stainless and acid-resistant steels, as the majority of steels for other purposes, have good or satisfactory technological properties: machinability by cutting, deformability in the hot and cold states, weldability, etc.

1. BASIC PRINCIPLES OF CREATING CORROSION-RESISTANT STEELS AND ALLOYS

A number of special works [485, 489, 488, 776, et al.] have been devoted to questions of the theory of corrosion. We shall thus touch only upon the basic principles, a knowledge of which is essential for elucidation of the nature of the effect of alloying elements and the structure of an alloy, which effect in turn determines the means of creating corrosion-resistant steels and alloys, chiefly ferrous ones.

A distinction is made between chemical and electrochemical corrosion. A particular case of chemical corrosion, in which the metal or alloy interacts directly with the medium, is gas corrosion at high temperatures, which determines the degree of corrosion resistance of the steel or alloy. Steel is also subjected to chemical corrosion in pure, dry air. The latter case, however, is extremely rare. In reality, air usually contains various impurities and moisture. Hence atmospheric corrosion is, as a rule, a variety of

electrochemical corrosion, which includes the majority of the most important forms of corrosion with which it is necessary to deal when steel comes in contact with the solutions of different acids, alkalis, and a number of other liquid media.

Of the varied types of corrosion attack on metals and alloys, the most unfavorable is local corrosion, which includes spot corrosion [*korroziya pyatnami*], pitting corrosion [*tochechnaya korroziya*], and intercrystalline corrosion. Intercrystalline corrosion is especially dangerous, since a sharp deterioration of the mechanical properties of the alloy is observed at the same time in this case.

In chemical corrosion a film is formed on the surface of the metal which under certain conditions may play a protective role by impeding further contact between the metal and the medium. In a particular case of oxidizing processes, but the one which is the most important for practical application, the film forming on the surface of the metal or alloy consists of oxides of the metal or various components of the alloy. At room temperature the rate of diffusion of the oxygen from the medium through the oxide film, as well as that of the atoms of the metal or alloy components in the opposite direction, is negligibly low. Hence the thickness of the protective film under these conditions is extremely small and ranges for various active metals (Al, Fe, Cr, Ni, et al.) from 20 to 50 $\overset{0}{\text{Å}}$. According to some sets of data, the film thickness on acid-resistant steel is 10 to 50 $\overset{0}{\text{Å}}$, and according to others it may be much greater, depending on the quality of surface polishing. In all cases the oxide film is colorless and transparent, but due to the absence of diffusion it may have a protective effect even at such small thicknesses, if it possesses adequate density and resistance to the action of the medium in question.

A protective layer is also formed on a number of metals such as iron, nickel, cobalt, chromium, and others when they are acted on by certain

oxidants. This imparts to them a high chemical resistance to the very same oxidants over a wide range of concentrations of the latter. This effect, which is termed passivation of metals, is most often accompanied by increase in their electrode potential. In certain metals such as chromium, the electrode potential hereupon becomes positive in place of negative and close in value to the oxidation-reduction potential of the medium. Hence these metals are, so to speak, transformed from base metals into noble metals for definite conditions. The tendency of the corresponding metals to develop passivity is preserved to one extent or another even when they form part of alloys.

The nature of the artificial protective layer which forms on metals upon passivation has not as yet been fully ascertained. According to the hypothesis of Faraday and the theory developed by Academician V. A. Kistjakovskiy, this protective layer also represents a very thin oxide film. According to another theory, the oxygen adsorbed by the surface layer of the metal has a catalytic protective effect. Even metals and alloys which do not form oxides under these conditions, such as platinum in a solution of hydrochloric acid [780], may become passive according to the second mechanism. There is still disagreement among the experimental data for certain metals and alloys. In particular, electron diffraction studies [779] have shown for iron that an oxide film is formed on it upon passivation which consists of extremely fine small crystals of cubic $\gamma\text{-Fe}_2\text{O}_3$. But the opinion has also been advanced that this oxide film is in the amorphous state. Studies by the conductivity method [781], on the other hand, indicate that the passive state of iron is due to the formation on its surface of a very fine and unstable adsorbed layer of oxygen. Data are available for stainless chromium steels justifying the assumption that the basic reason for their stability in oxidizing media is also the formation of an adsorbed layer of oxygen [785]. It has been shown in another paper [791] that there is an oxide film on passive stainless steel, but the hypothesis is advanced

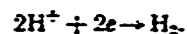
of the simultaneous presence on it (under the film and in the pores) of an adsorbed layer of oxygen as well. It is not a question here of "weak" physical adsorption, but of chemical sorption, deep implantation of the oxygen in the metal. This hypothesis is the most probable one for many cases and is gaining increasingly wider acceptance at the present time [779]. In particular, it is precisely by a combination of phase and adsorption films that one can explain the not simply the high stability of the passive state of stainless steels, which distinguishes them from iron, despite the fact that the thickness of the protective film on stainless steels and iron is practically the same.

The composition and structure, and hence the protective properties as well, of the oxide film which forms in air and in oxidizing media on the surface of alloys depends on the composition of the alloys. On chromium steel the film is enriched with chromium oxide. Only chromium oxide was found, in addition to ferric oxide, in the film of a steel containing 16% Cr and 8% Ni, its quantity varying over a wide range and reaching 90%. 53% Fe_2O_3 ; 32% Cr_2O_3 and 12% NiO were found in the isolated film of the same steel containing molybdenum. Nickel oxides were absent from the film in all cases. A film enriched with chromium oxides, apparently in combination with an adsorption layer, imparts the best protective properties to ferrous alloys.

Electrochemical corrosion of metals and alloys, which occurs in solutions, is a process of electrochemical oxidation, i. e., oxidation accompanied by disruption of the electric neutrality and by the occurrence of a potential jump on the metal-solution boundary. Ions of the metal partially migrate from the crystal lattice into the liquid phase, since this leads to reduction of the free energy of the system. The values of the normal or standard electrode potential, which is the equilibrium potential of a metal when the activity of its own ions in solution equals unity, may serve as a relative char-

acteristic of the change in free energy upon the oxidation of various metals, and hence of their thermodynamic stability as well. Table 101 [197, 778] gives for certain metals the values of the standard potential according to the galvanic series whereby the potential of the hydrogen electrode is taken as zero. For metals tending toward passivation, the potentials correspond to their active state.

The process of oxidation of the metal should cease upon achievement of the equilibrium potential, which corresponds to the free energy minimum of the system. However, the equilibrium potential is not reached, and the process of electrochemical corrosion continues if a reduction or cathodic process (cathodecdepolarization) occurs simultaneously with the oxidizing or anodic process. The cathodic process may consist in the reduction of many substances [cf. 778, Table 2], particularly of the ions of another metal or of oxygen contained in the solution. A necessary condition for this is negative total change in the free energy of the system, i.e., the reduced metal must have a more positive equilibrium potential than the dissolved metal (in the case of a reduction process, the potential sign should be taken which is opposite that given in Table 111 for the oxidation process). In the most important particular case, oxidation, such as of iron and its alloys, occurs through the reduction of hydrogen ions:



In examination of the mechanism and kinetics of the process of electrochemical corrosion, the theory of microelements developed in the Soviet Union by the school of G. V. Akisov [485, 776, et al.] proceeds from the fact that the anodic and cathodic processes are localized in individual microsections (the heterogeneous-electrochemical mechanism). According to this theory, the surface of a metal or alloy acquires unlike potentials at all its points

Table 101

Normal Electrode Potentials of Certain Metals

Metal and oxidizing reaction	Potential, v	Metal and oxidizing reaction	Potential, v
$Mg \rightarrow Mg^{++} + 2e$	-2.37	$Sa \rightarrow Sa^{++} + 2e$	-0.135
$Be \rightarrow Be^{++} + 2e$	-1.85	$Pb \rightarrow Pb^{++} + 2e$	-0.126
$Al \rightarrow Al^{+++} + 3e$	-1.66	$Fe \rightarrow Fe^{++} + 2e$	-0.036
$Ti \rightarrow Ti^{++} + 2e$	-1.63	$H_2 \rightarrow 2H^{+} + 2e$	0.000
$Mn \rightarrow Mn^{++} + 2e$	-1.18	$Cu \rightarrow Cu^{+} + e$	+0.337
$Zn \rightarrow Zn^{++} + 2e$	-0.763	$Cu \rightarrow Cu^{++} + 2e$	+0.521
$Cr \rightarrow Cr^{+++} + 3e$	-0.74	$2Hg \rightarrow Hg_2^{++} + 2e$	+0.769
$Fe \rightarrow Fe^{++} + 2e$	-0.440	$Ag \rightarrow Ag^{+} + e$	+0.799
$Cd \rightarrow Cd^{++} + 2e$	-0.403	$Hg \rightarrow Hg^{++} + 2e$	+0.854
$Co \rightarrow Co^{++} + 2e$	-0.277	$Pd \rightarrow Pd^{++} + 2e$	+0.987
$Ni \rightarrow Ni^{++} + 2e$	-0.250	$Pt \rightarrow Pt^{++} + 2e$	+1.2
$Mo \rightarrow Mo^{+++} + 3e$	-0.20	$Au \rightarrow Au^{+++} + 3e$	+1.50

upon coming in contact with a liquid medium, under the influence of various factors such as multiple-phase structure of the alloy, impurities and stressed sections, inhomogeneity of the protective films and liquid medium, etc. Galvanic macroscopic or microscopic area (elements) consequently arise, and the anodic sections are destroyed.

However, the decisive role in the course of the corrosion process is frequently ascribed erroneously to the action of galvanic elements. In reality, as has been demonstrated by a number of studies [778], the origination of galvanic elements is only one of the possible ways of transition of a system to a thermodynamically stabler state, which transition is more advantageous from the standpoint of energy and leads to further acceleration of the corrosion process. Moreover, as demonstrated by A. I. Shultin [626, 782], the corrosion process may take place even when the potential is fully identical at all points of the surface of the metal. The presence in the metal or alloy of cathodic sections, on the other hand, may accelerate the process because of the fact that in these sections the activation energy of hydrogen

precipitation is lower, or, what is the same thing, the overvoltage of the hydrogen reduction reaction is lower. The hydrogen overvoltage, other conditions being equal, depends on the nature of the metal [197, 867] and is related, in particular, to its ability to absorb oxygen.

The role of the resistance factor in the rate of progress of the corrosion process in operation of the microelements in electrolytes is at any rate very small. But the role of the resistance factor is considered to be substantial under conditions of formation of macroelements [175]. A calculation carried out by A. I. Skultin [182], on the other hand, has shown that the role of the ohmic resistance of a solution, even assuming considerable localization of the anodic and cathodic processes, is very small: the "kinetic weight" of this factor is less than ten percent. Hence to describe the process of corrosion and its kinetics, use may be made only of polarization curves which reflect the role of the determining factors of the process.

As an illustration, which we shall require further on, Figure 358 [182] gives diagrams of polarization curves (depicted by straight lines for the sake of simplification) for the case of corrosion of two-phase alloys. The equilibrium potentials striving to establish themselves in the electrolyte in question on each phase are φ_1 and φ_2 , and lines 1 and 2 show the change in the anode current for each of the phases. The line of the cathode currents 3 starts from the point corresponding to the equilibrium oxidation-reduction potential of the solution φ_3 . If the overvoltage of the reduction reaction is the same, the stationary potential φ'_{st} is established in the system (Fig. 358a). Phase 1 will hereupon corrode at the rate $i_1 = i_2$, while phase 2 is cathode polarized ($\varphi'_{st} < \varphi_2$) and will not corrode. If the overvoltage of the reduction on phase 2 is smaller than on phase 1 and is represented by line 4, which starts from the same point, φ_3 , the stationary potential φ''_{st} is established. The rate of corrosion of the first phase will hereupon rise and will be proportional to $i_2 = i_4 + i_5$, but the

cathode current will be distributed over both phases: current i_4 for the second phase and current i_5 for the first. Line 5 shows the total reduction rate on both phases.

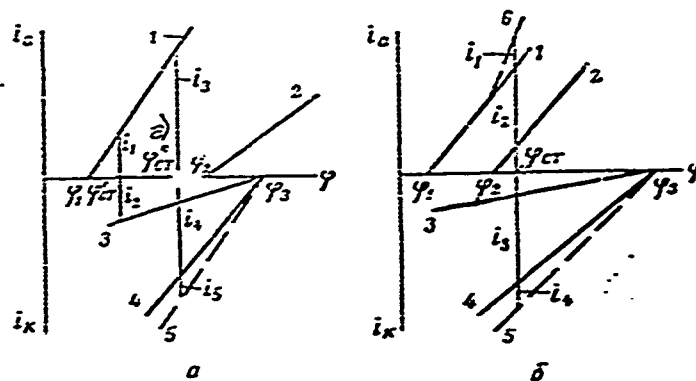


Figure 358. Diagrams of polarization curves for the case of corrosion of two-phase alloys.

(a) φ_{st} .

The diagram of Figure 358b corresponds to the case in which the anode current as well is distributed over both phases of the corroding alloy. As in Figure 358a, line 5 here shows the total cathode currents and line 6 the total anode currents. In this case the stationary potential φ_{st} , which corresponds to the current equation $i_1 + i_2 = i_3 + i_4$ will be established in the system. Both phases of the alloy will hereupon fail; phase 1 at the rate i_2 and phase 2 at the rate i_1 , current i_5 of the total cathode current falling to phase 2 and current i_4 to phase 1.

From the standpoint of creation of alloys which are stable in one medium or another, a very important part is played by auxiliary processes which cause the rate of the corrosion process to decrease, or inversely in certain cases to increase, in comparison with the rate determined by the polarization curves in Figure 358. Numerous studies show that these processes are related to the formation or destruction of the passivating film or to the formation of a difficultly soluble dense layer of corrosion products.

The passivating film, the nature of which was discussed earlier, slows down corrosion chiefly through retardation of the anodic process, by preventing passage of the ions of the metal into solution. Such a film is formed on a number of metals and alloys in oxidizing media, for example, in concentrated solutions of sulfuric acid or in solutions of nitric acid, etc. However, the corrosion rate rises sharply with high concentrations of nitric acid. This phenomenon, which has been given the designation "overpassivation", has been observed on carbon and chromium-silicon steel, on chromium, on stainless steels, and in various media. We shall not deal with the assumed causes of overpassivation; it is discussed in special literature [865, 865, 776].

The great acceleration of the process of steel corrosion is caused by the presence in the solution of halide ions, particularly chlorine ions, such as form upon the addition of hydrochloric acid to nitric acid, in the corrosion of steel in sea water, etc. This is ascribed [867] to displacement of oxygen from the double electric layer at the surface of the metal and to destruction of the passivating film. The chlorine ion is also greatly activated by solution of chromium in sulfuric acid. However, the introduction of a certain amount of chlorine ions into sulfuric acid in a number of instances not only does not accelerate, but on the contrary greatly retards, the process of corrosion, especially of chromium-nickel steels of the 25-20 and 18-8 types and of chromium steels containing up to 17% Cr. The corrosion of chromium steel containing 27% Cr, on the other hand, is greatly intensified in this case [864].

The processes which affect the solution of metals also include the difference effect. It consists in the fact that the rate of self-solution decreases in some cases (positive difference effect), and increases in others (negative difference effect), with increasing anodic polarization. The negative difference effect was observed previously only with respect to aluminum and magnesium alloys, but has recently been established also [866] for

18X18N9T steel in solutions containing chlorine ions; and for the first time it was registered in the progress of the corrosion process as a result of oxygen depolarization. It was demonstrated in this case that destruction of the passive film, which is restored when the anodic polarization is removed, takes place in solutions containing chlorine ions. However, this effect is of less importance for the process of corrosion of stainless steels than it is for aluminum and magnesium alloys.

Thus, it follows from the foregoing discussion, and particularly from Figure 358, that to obtain corrosion-resistant steels it is necessary to alloy the steels with such elements as form solid solutions with iron and which themselves possess high chemical stability in a given medium, either because they have a positive electrode potential (Table 101), i.e., are thermodynamically stable, or because they tend toward passivation in this medium. The most important of the alloying elements which meet this requirement, for the case involving the action of oxidizing media, is chromium, which acquires a positive potential as a result of passivation. Hence chromium is introduced into the majority of corrosion-resistant steels. On the other hand, in order to impart to steel a chemical resistance to the action of non-oxidizing media, when passivation cannot be utilized, it is necessary to alloy the steel with elements which are thermodynamically stable in these media. In the case of action of dilute sulfuric acid, such elements are, for example, nickel and silicon. Certain other elements will be dealt with further in the discussion.

The alloying of steel with elements which contribute to the formation on the surface of a difficultly soluble and dense layer of corrosion products exerts a slight effect and is utilized chiefly to achieve a certain increase in the resistance to atmospheric corrosion. As an example we may cite the introduction of copper into low-alloy structural steels ([Russian] p. 360). Little study has as yet been devoted to the possibilities of alloying steel with elements which are capable of raising its chemical stability by increasing the

overvoltage of the hydrogen reduction reaction.

The amount of the alloying element dissolving in the iron which must be introduced into the steel to impart a high chemical stability to it in a given medium is determined basically by the principle established by G. Tamman [487] and known as the " $n/8$ mole law".

The essential feature of this principle is, as is known, that when a nobler metal is added to a less noble one the effect of the former is exerted intermittently at a concentration corresponding to $n/8$ mole, i. e., 12.5; 25; 37.5, 50 ... % (atomic). These concentrations, which Tamman calls boundaries (or thresholds) of chemical stability, differ not only in different systems, but may even differ in the same system when acted upon by different aggressive media.

The existence of boundaries of chemical stability has been established in a large number of alloys consisting of solid solutions, but deviations from this principle are also observed. In particular, it is difficult to consider the rise in chemical stability at the respective boundaries in a number of systems as intermittent. In certain alloy-medium systems the first boundary at $1/8$ -mole concentration is scarcely manifested at all. One may cite as an example iron-silicon alloys, in which the boundary of chemical stability in nitric and sulfuric acids corresponds to a silicon content of no less than $2/8$ mole (14.5%). Although the boundary is manifested at $1/8$ mole in other systems, it is relatively faint. Thus, the stability of iron-nickel alloys in solutions of sulfuric acid in a concentration of up to 20%, as is to be seen from Figure 359 [869], increases appreciably with a content of $1/8$ mole (15.5%) Ni, but does so the most abruptly with $2/8$ mole (27%) Ni. This raises practical difficulties, which in the examples referred to amount to the necessity of alloying the steel with a large amount of costly nickel and to limiting the use of iron-silicon alloys strictly to cast alloys, which moreover, are very brittle and prone to crack formation (siliceous cast iron, thermal

stances). It is to be seen at the same time from Figure 359 that the increase in stability at $1/8$ and $2/8$ mole can only arbitrarily be considered intermittent. The same is true of iron-silicon alloys, ferrochromium alloys in nitric acid (cf. Fig. 362), and others.

There are several explanations of the $n/8$ mole principle. The explanation given by Tazman himself relates this effect to the ordered arrangement of the atoms in the solid solution lattice. With this explanation it is assumed that in an alloy with a concentration of $n/8$ mole of the noble component, planes appear which are so enriched with its atoms that the destructive effect of the medium is greatly weakened when it comes in contact with the first such plane. However, one can scarcely expect an ordered arrangement of the atoms at a concentration of $n/8$ mole of the added element in all systems, and such arrangement is not confirmed by the change in atoms' other properties with change in the concentration and by X-ray diffraction analysis. This may to a certain extent explain the observed deviations from the principle, as well as the circumstance that in a number of systems the increase in stability at the corresponding boundaries may only arbitrarily be considered intermittent. On the other hand, even the insufficiently pronounced jump in chemical stability at the boundaries, and the very deviations from the principle, can scarcely be explained if one proceeds from an entirely statistical arrangement of the atoms of the dissolved component in the solid solution.

The principle and the observed deviations from it could have been ascribed to the fact that at the initial moment the process of corrosion proceeds selectively and that this leads to enrichment of the surface planes of the alloy with atoms of the protecting element. But even such an hypothesis as this is not always confirmed by experiment, for example, in a lead-mercury system [488], in general corrosion of ferrochromium alloys [881], etc. Enrichment of the surface layer of an alloy with a noble ele-

but has nevertheless been observed in a number of studies to the point where in certain alloys (such as copper-gold) this layer consisted only of the atoms of the latter. This important circumstance may be the result of secondary electrochemical exchange between the noble and base components of the alloy (see [Russian] p. 612 and [417]).

It seems to us that in explaining the boundaries of chemical stability one should proceed from the modern concepts given in the chapter dealing with the phases formed by elements in steel ([Russian] p. 44). According to these

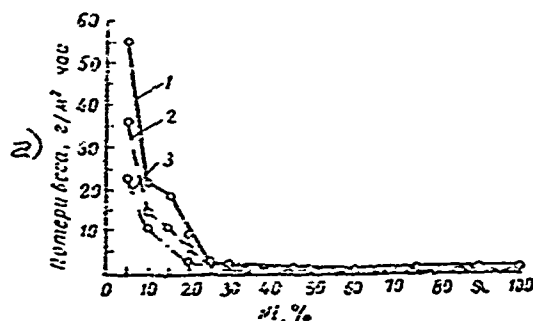


Figure 359. Corrosion of iron-nickel alloys in sulfuric acid at 60°C. Length of test period 100 hours:

1 - 20 percent H_2SO_4 ; 2 - 10-percent; 3 - 5-percent:
(a) weight loss, g/m^2 .

ideas, there is present in the solid solution a selective adjacency of dissimilar atoms which is determined by their chemical interaction. In combination with the "geometric" factor, this permits the atoms of the noble element -- when it is contained in the solid solution corresponding to the stability boundary -- to block a certain group of atoms of the base component from the aggressive action of the given medium, or to subject them to the influence of the passivating film. It is probable that upon the reverse displacement of atoms of the noble element from the solution and enrichment of the surface layer with them, the principle of selective adjacency, which is determined by the chemical interaction of the atoms, is again maintained. With such an

approach as this, it is even possible to assume that the very existence of the Nernst principle attests once again to the presence of selective adsorption of atoms in the solid solution.

Redetermination of the structure creates the basic prerequisite for lowering of the corrosion resistance of an alloy as compared with a homogeneous solid solution. In fact, it follows from Figure 558 that the presence of a second, cathodic phase may accelerate corrosion of the basic mass through decrease in the overvoltage of the cathodic reaction on this phase (lines 4 and 5). However, it is to be seen from this same Figure 558 that there will be no such effect if the overvoltage of the cathode reaction on both phases is approximately the same (lines 3). Alternatively, this effect will be slight if the difference in the values of the overvoltage on both phases is small, i.e., the inclination of line 4 differs little from the inclination of line 3 toward the X-axis. Hence the widespread concept of the lower corrosion resistance of heterogeneous alloys does not always agree with the actual state of affairs. At any rate it cannot be considered to be a rule, as this has, in fact, been noted quite some time ago [486].

N. D. Tomashov and others [178, 869] have recently given theoretical substantiation to the possibility of lowering the corrosion rate under the effect of formation of or increase in cathodic impurities in an alloy. According to their hypothesis, the presence of cathodic inclusions under conditions favoring the establishment of a passive state (when the anodic phase tends toward passivation and there are no activators -- chlorine ions -- in the corrosive medium) may, through increase in the anodic polarization of the basic anode background in the structure, cause the alloy to pass into a stable passive state, as this was observed by them upon anodic polarization through an external source of light. The authors support their theoretical conclusions with the following experimental results. Figure 560 [870] shows the great reduction in the rate of corrosion of Kh15N9 steel in sulfuric acid of various

concentrations under the effect of alloying with "cathodic admixtures": platinum, palladium, and copper. Shown in Figure 361 are the potentials of these steels after corrosion tests in comparison with the potentials of pure metals, platinum, palladium, copper, and chromium. They obtained a similar effect with chromium steel containing 27% Cr in solutions of sulfuric, formic, and oxalic acids. A new principle of alloying chemically stable steels is proposed on this basis.

These data are undoubtedly of great interest. It is still not clear, however, why the elements referred to above form cathodic phases in an alloy and whether they do so at all. Since they are all in the solid solution, their role may also be interpreted from the standpoint of the general theory on the effect of solute elements possessing high thermodynamic stability in a given medium. As for the mechanism of their effect even in relatively small quantities, it may be assumed, for example, that in media in which the steel is located on the boundary of the active and passive states, the elements in question act with respect to the layer enriched with chromium and nickel in the same way as chromium and nickel themselves act with respect to the iron matrix. After a certain period of time from the beginning of corrosion, the surface planes, apparently, are enriched with the atoms not only of nickel and passive chromium (according to the authors' experiments, chromium becomes self-passivated in 30-percent H_2SO_4 ; its potential equals +1.07 v), but also of the noble metals introduced into the alloy, whereupon their auxiliary protective effect is manifested. The existence of such mechanism is indirectly evidenced by the fact reported by the authors that 27-percent chromium steels with noble-metal admixtures were passivated in a few minutes, and chromium-nickel steels as late as 1 to 3 days after the beginning of the test. This possibly explains the fact that the potential of the steel tested (Fig. 361), after its palladium contents was increased, approached the potential of palladium itself. On the other hand, in steel alloyed with copper, the potential

after testing was more positive than in copper itself, apparently because of the formation of a dense layer of corrosion products.

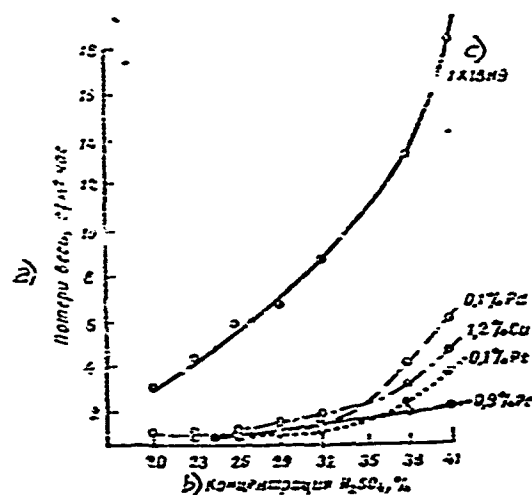


Figure 360. Rate of corrosion of 1Kh18N9 steels alloyed with platinum, palladium, and copper, as a function of concentration of H_2SO_4 at 20° . Length of test period 360 hours. (a) weight loss, $g/cm^2/hour$; (b) concentration of H_2SO_4 , %; (c) 1Kh18N9.

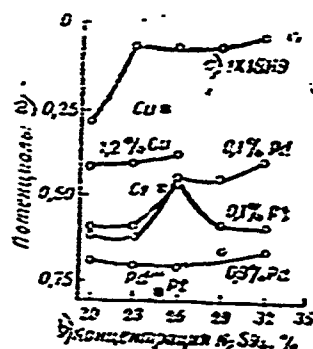


Figure 361. Potentials of 1Kh18N9 steels alloyed with platinum, palladium, and copper at the end of corrosion tests in H_2SO_4 at room temperature:

\square - potentials for pure metals indicated in 25-percent H_2SO_4 ;

(a) potentials; (b) concentration of H_2SO_4 , %; (c) 1Kh18N9

The very process of enrichment of the surface layer with the noble elements contained in the steel may proceed, as in general in solid solutions, in accordance with the "secondary electrochemical exchange" mechanism proposed by V. V. Skorochelleti and A. I. Shultin [468, 417] for copper, molybdenum, silver, mercury, and others. This hypothesis is also advanced by the authors in one of their papers [570] and is confirmed to a certain extent by the positive effect achieved upon the introduction of ions of noble metals into the

solution [416, 679].

Of great importance for the corrosion resistance of heterogeneous alloys are the location and extent of dispersion of the phases. The location of certain phases along the grain boundaries of an alloy may cause intercrystalline corrosion, which will be discussed in greater detail later on. The effect of the extent of dispersion of the phases is not well defined [486]. Increase in the extent of dispersion mostly intensifies the corrosion of an alloy. This may be ascribed to the increase of the total area on which the corrosion process is accelerated due to adjacency of the second phase. However, in a number of cases a high extent of dispersion may also prove to be a positive factor, because of the decreasing permeability of the alloy to the action of the medium, the widening area of action of the protective film, etc. The minimum chemical stability of an alloy sometimes corresponds to a certain "critical" extent of dispersion. Thus, upon the solution of quenched and tempered carbon steel containing 0.95% C in 1-percent sulfuric acid, the maximum solubility was observed after tempering at 400° [cf. 871]. The authors gave the structure of such steel the name "osmondite", which, however, was not subsequently adopted.

The corrosion resistance of a steel or alloy may be greatly affected by other factors in addition to the chemical composition and structure. Thus, for example, auxiliary and residual stresses and plastic deformation of steel increase the rate of its corrosion, this being accompanied by lowering of the electrode potential [489]. Corrosion in this case frequently acquires an intercrystalline nature, and this is especially dangerous. Annealing relieving residual stresses and the results of plastic deformation restores to the steel the corrosion resistance inherent in it with the given composition.

The acceleration of the corrosion of an alloy under the influence of stresses and plastic deformation should not, however, be confused with the phenomena of corrosion cracking and corrosion fatigue. Intensification of

the corrosion process under the action of stresses is observed with any stressed state of an alloy. Corrosion cracking, on the other hand, is brittle failure of an alloy acted on by an aggressive medium, failure caused by normal tensile stresses. Even alloys having a high general corrosion resistance are subject to corrosion cracking. Corrosion fatigue, which is observed when an alloy is acted upon simultaneously by the corrosion process and alternating stresses, is also mechanical in nature and is characterized by the absence of a definite value of the fatigue limit and by high dependence of the fatigue strength on the frequency of the cycles. Preliminary corrosion, on the other hand, simply lowers the fatigue limit of an alloy as a result of the damage it causes [76]. Thus, neither corrosion cracking nor corrosion fatigue has a direct bearing on our subject.

The quality of the surface of a steel has a substantial effect on corrosion resistance. After coarse machining the active surface is greater and the overvoltage of hydrogen precipitation is lower than after polishing, and the corrosion resistance is accordingly higher in the latter case. Thus, for example, for 5Kh15 steel containing 0.26% C and 14.1% Cr, on plates subjected to machine grinding which thereafter had a coarse surface, upon dissolution in a 5% sodium-chloride solution, losses were obtained [78] which were almost a whole order of magnitude larger than on plates ground and finished by hand. Substantial increase in corrosion resistance was observed on a steel with 0.06% C and 14% Cr in a vapor medium after electrolytic polishing in comparison with conventional machine polishing [76]. It has also been shown with a chromium-nickel steel of the 18-8 type [78] that in the event of electrolytic polishing in baths of varying composition the surface is passivated in different ways and possesses a varying corrosion resistance. Improvement of the condition of the surface of steel in proportion to its dissolution, for example removal of scale and impurities by sandblasting, etc., thus leads to

retardation of the corrosion process. However, in highly aggressive media an increase was observed /572/ in the initial rate of corrosion of stainless steel with increasing degree of surface finish. This was, apparently, due to the presence of a work hardened layer. The corrosion rate became constant after removal of the deformed layer and baring of the unaffected mass of metal.

2. ROLE AND EFFECT OF ALLOYING ELEMENTS AND CARBON IN STAINLESS AND ACID RESISTANT STEELS

Alloying must provide for different properties of steel, depending on the conditions of employment of the latter. But since these properties obey various laws, it is not always possible to obtain the desired combination of all properties in one steel. This is particularly true of the possibility of utilizing carbon, which, generally speaking, affects the corrosion and mechanical properties in different directions. The same may be said of the structure and the heat treatment conditions. Austenitic steels possess a higher corrosion resistance and in a larger number of media, but display lower strength values (particularly the yield point) at room temperature than do ferritic-martensitic steels. At the same time, they possess a high plasticity and ductility and valuable auxiliary properties: they are non-magnetic, have a high electric resistance, and are highly heat-resistant. We shall thus discuss separately the effect of alloying elements and carbon on the corrosion, mechanical, and technological properties of ferritic-martensitic and austenitic steels.

A. THE ROLE OF ALLOYING IN INCREASING THE TOTAL CORROSION RESISTANCE

Ferritic-martensitic steels

It follows from what was stated earlier about the basic principles that chromium is the alloying element which increases the corrosion resistance the most effectively in oxidizing media. Chromium transmits to steel its tendency toward passivation when its content exceeds 12 to 13%. This is the quantity of chromium which has been established as its minimum content in a steel which is stable in the atmosphere and in oxidizing acids. Further increase in the chemical stability of steel in the media referred to, as well as communication to it of increased resistance to certain new media, may be achieved

by augmenting the chromium content, which may be raised to 26 to 30%.

Subsequent studies have shown that the minimum content of chromium in corrosion-resistant steel also conforms in the main to the $n/8$ mole law, although the increase in resistance at the respective boundaries may only arbitrarily be considered intermittent even in this case, as is to be seen from the spread of the points in Figure 362 [417]. Deviations from the $n/8$ mole law in commercial ferrochromium alloys are also possible because of the fact that binding of chromium in carbides reduces the content of the latter in the solid solution.

The amount of carbides is the greater, and hence the extraction of chromium from the solid solution is the more extensive, the higher is the carbon content of the steel. It is for this reason that the corrosion resistance of chromium steel drops with increasing carbon content, as may be seen, for example, from Figure 363 [491]. The negative effect of carbon on the corrosion resistance of steel may be compensated by increasing the chromium content of the latter to a level such that a sufficient quantity of it remains in the solid solution. This quantity may be estimated roughly on the basis of the $n/8$ mole law and the composition of the carbide. Thus, with an average content of 0.1% C, of steels containing ~13, 15, and 17% chromium the latter possesses the greatest stability in nitric acid at 20°¹. Approximately the same stability is possessed by steel containing 0.5% C but about 30% Cr. The highest stability is exhibited by a steel with ~0.1% C and 27% Cr, this corresponding to $2/8$ mole. The steel with 30% Cr, even when containing 1 to 1.5% C still possesses a corrosion resistance which is satisfactory for many technical purposes, despite the presence in it of a very large amount of free carbides.

The possibility of changing the corrosion resistance of chromium steels

¹For detailed information on the chemical stability of diverse steels, see [492, 41, 769].

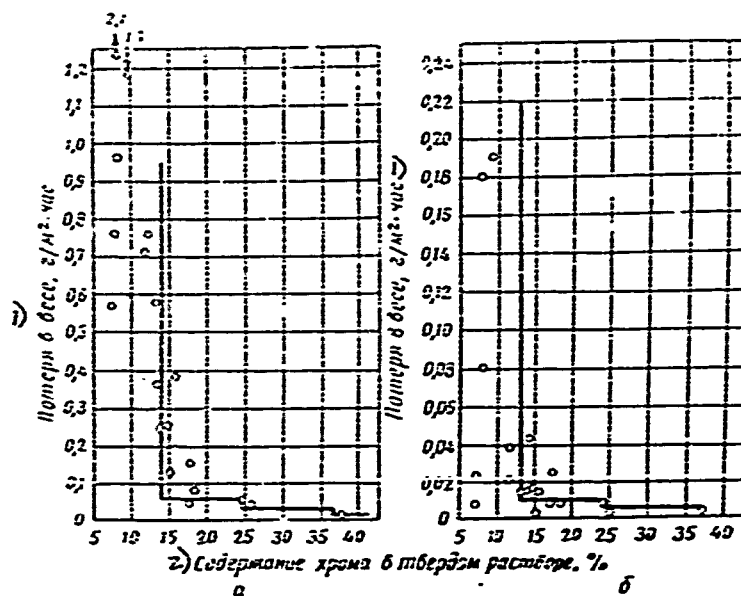


Figure 362. Corrosion of annealed chromium steels in 50-percent HNO_3 :

a - at 90°; b - at 50°;

(1) - weight loss, $\text{g}/\text{m}^2/\text{hour}$; (2) Chromium content of solid solution, %.

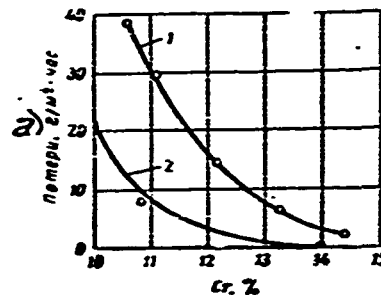
by means of heat treatment in which the quantity and extent of dispersion of the carbides are modified depends on their chromium and carbon content according to the structural diagram. As may be seen from Figure 364 [borrowed from Adcock], in carbon-free alloys the gamma region is closed off at 11 to 12% Cr. Consequently, all practically carbon-free alloys containing over 11 to 12% Cr are ferritic steels. With the introduction of carbon into the alloys, the maximum chromium content at which the gamma region is closed off rises appreciably. A ternary Fe-Cr-C system has been studied by many authors, whose data disagree somewhat. Some idea of the structural regions in the ternary system is afforded by the diagram given earlier in Figure 41. As may be seen from the diagram, in order for steel to be receptive to martempering it must contain either no more than 12 to 14% Cr with a low carbon percentage or no less than $\sim 0.5\%$ with 17 to 18% Cr. A steel containing over 25% Cr is not recep-

tive to martempering, even with a large quantity of carbon.

Chromium steels which are receptive to martempering possess the highest corrosion resistance in the hardened state, when the carbides have been transferred to the solid solution. Subsequent tempering, in which the decomposition of martensite is accompanied by precipitation of the carbides, lowers the corrosion resistance. Since the martensite in these alloys possesses an increased stability toward tempering, perceptible lowering of the resistance begins at $\sim 400^{\circ}$. However, tempering at temperatures above $\sim 600^{\circ}$, as may be seen from Figure 365 [491], for example, again elevates the corrosion resistance, although its value corresponding to the hardened state is usually not reached. Hence, from the standpoint of corrosion resistance it is better to subject chromium steels for structural purposes to high tempering.

Figure 365. Effect of carbon on the corrosion of chromium steels in nitric acid:

1 - 0.51 to 0.55% C; 2 - 0.09 to 0.16% C;
(a) Losses, $\text{g}/\text{m}^2/\text{hour}$.



This course of change in corrosion resistance upon tempering is apparently the result of several processes. The first of them, which is manifested up to the stability minimum on the curve, consists in impoverishment of the basic mass in chromium. This factor may play a particularly important part if the amount of chromium remaining in the solid solution after precipitation of the carbides is below the chemical stability boundary. The increase in chemical stability after high tempering is explained in part by coagulation of the carbides. It may be assumed on the basis of the diagrams of Figure 359 that coagulation leads to reduction of the total surface on which the process of corrosion is accelerated through contact between the main mass and the

carbide phase. The positive role of coagulation of the carbides is confirmed indirectly by the maximum solubility, referred to above, of carbon steel upon tempering at 400° , when the coagulation factor is the only one, since both the composition of the carbide and the composition of the basic mass scarcely change at all in this case.

But change in the composition of the carbide may also exert a great effect in chromium steels, in addition to coagulation. Some hold [41] that upon high tempering there occurs a transformation of Cr_{23}C_6 into the carbide

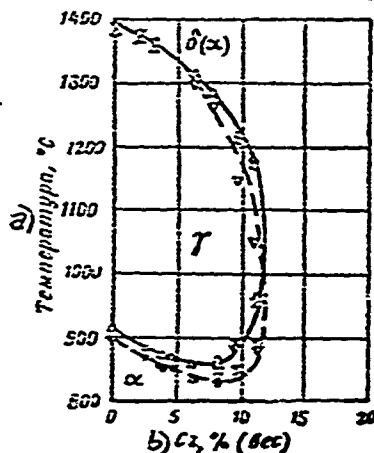
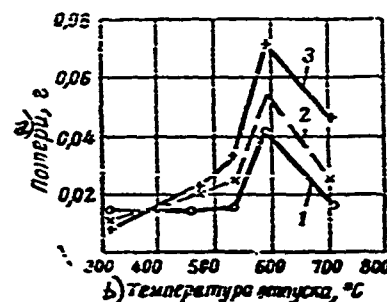


Figure 364. Gamma region in structural diagram of a Fe-Cr system (according to Adcock). Thermal analysis: Δ -heating; ∇ -cooling; Dilatometric analysis: \blacktriangle -heating; \blacktriangledown -cooling; (a) Temperature, $^{\circ}\text{C}$; (b) Cr, % (by weight).

Cr_7C_3 , which binds less chromium. In reality, however, it is to be expected on the basis of thermodynamic and kinetic premises (cf. p. 174 and Fig. 108) that with elevation of the tempering temperature transformation of the carbide in the opposite direction will occur. It has also been demonstrated experimentally with a steel containing 0.18% C and 12.7% Cr [605] that in the process of tempering after quenching from 1025° the carbide composition changes in the sequence $(\text{Fe}, \text{Cr})_3\text{C} \rightarrow (\text{Cr}, \text{Fe})_7\text{C}_3 \rightarrow (\text{Cr}, \text{Fe})_{23}\text{C}_6$. It may, thus be assumed that the change in the composition of the carbide in the process of tempering affects the rate of the corrosion process also as a result of change in its equilibrium potential in a given medium, in conformity with

Figure 360. Such an assumption also means that the negative role of the carbides in general is probably not limited to extraction of chromium from the basic mass but is also related to the different values of the equilibrium potential and overvoltage of hydrogen precipitation of the carbides and of the solid solution.

Figure 365. Effect of quenching and tempering temperature on the corrosion resistance of a steel containing 0.57% C and 14.5% Cr:
1 - quenching from 925°; 2 - from 1040°; 3 - from 1150°;
(.) losses, g; (b) tempering temperature, °C.



According to the data of various sources, the quenching temperatures of chromium steels for the purpose of increasing their corrosion resistance vary (from 950 and even 900° to 1100°; the lower temperatures refer to steels with a lower carbon content). This is explained not only by the high sensitivity of corrosion tests to the test conditions, condition of the surface of the specimens, etc., but apparently also by the fact that the optimum quenching temperature must depend on a number of factors. In the quenched state, the corrosion resistance of steel must be the higher, the more completely have the carbides been converted to solution, i.e., the higher is the quenching temperature. It is apparently for this reason that steels with a higher carbon content must also have a higher quenching temperature. This effect of the quenching temperature must be retained after tempering until appreciable precipitation of the carbides from the martensite begins. At tempering temperatures above this, the opposite effect of the quenching temperature is to be expected, since the higher the latter and the smaller the amount of undissolved carbides remaining in the structure, the more strongly dispersed will be the carbides precipitated upon tempering. Precisely such a pattern as

this is to be detected in Figure 305. However, the difference in the weight loss (with specimens of the same dimensions) upon change in the quenching temperature within the 925 to 1050° range is small, after both medium and high tempering. The same was also found with 3Xh13 steel in certain other studies [704, 706].

In view of these circumstances, as well as the well-known effect which the nature of the working aggressive medium may exert, the quenching temperature should be selected in the 950 to 1050° range. Temperatures ranging from 950 to 975° considered the optimum for steels containing 0.25% C, and 975 to 1025° for steels with a higher carbon content. It is advisable to determine the optimum quenching temperature with greater precision by experiment, in conformity with the service conditions of the articles to be produced. It is necessary in this case to proceed above all from the necessity of ensuring the required characteristics of plasticity and ductility (see 634). These characteristics are much more sensitive to changes in the structure of the steel caused by variations of the quenching temperature than is the corrosion resistance. Semi-ferritic steels, such as those containing 17% Cr and 0.1% C, are subjected to annealing at a temperature of around 750°.

Austenitic and austenitic-ferritic steels

The introduction of increased amounts of nickel into high-chromium steels has led to the creation of steels of new types which have an austenitic structure and which possess a very high chemical stability in a large quantity of aggressive media. Of such steels, the widest use has been made of a steel containing 18% Cr and 8 to 10% Ni, designated abroad as 18-8 and in the Soviet Union as Kh18N9 (former brand designation EYa).

The increase in the chemical stability of chromium steel, particularly in nonoxidizing media, with the introduction of nickel into it is apparently due to a greater extent to the action of the nickel itself than to the forma-

nation of an austenitic structure. In fact, austenitic steels -- manganese and chromium-manganese varieties -- do not possess the same chemical stability as nickel and chromium-nickel austenitic steels. The austenitic structure, as a single-phase and denser structure, also plays a certain positive part in increasing the chemical stability of steel. However, this part should not be exaggerated, especially from the standpoint of the single-phase structure, as noted earlier.

Calculations show [cf. 427] that the optimum composition of austenitic chromium-nickel steels, as established empirically, also obeys the $n/8$ mole law in the main from the standpoint of their stability in certain media. This law normally determines the content of either chromium or the nickel, depending on which of these elements is itself chemically stable in a given medium. Thus, for example, the stability of steel in boiling sulfuric acid rises especially abruptly upon transition through $2/8$ mole nickel, while the chromium content has very little effect. When the steel is subjected to the action of nitric acid, its stability rises sharply with $n/8$ mole chromium, while the effect of the nickel does not conform to the law. The role of nickel in achieving an austenitic structure, on the other hand, remains unchanged in all cases. It is necessary to introduce no less than 8% Ni into a steel containing about 18% Cr in order to achieve this goal. Thus, it is frequently necessary to adopt a nickel content of over 8% in acid-resistant steel, if this element determines the boundary of chemical stability. The Kh18N9 steel, however, contains the minimum amount of nickel also out of economic considerations.

Figure 366a (borrowed from Krivobok) gives the pseudobinary structural diagram of the Fe-Cr-Ni-C system for a section containing 16% Cr and 6% Ni, and Figure 366b, the upper left corner of this section, studied in greater detail in later investigations. It is to be seen that with the carbon content customary for industrial steels of this type (up to 0.25%), their structure

in the equilibrium state consists of austenite, alpha phase, and carbides which are of the $(Cr, Fe)_{23}C_6$ type as in steel with the same quantity of chromium but with no nickel. The solubility of the carbon in the austenite at room temperature is 0.02 to 0.05% and changes with the temperature along the line SE. By means of quenching from temperatures located above this line, the carbon can consequently be held in the supersaturated solid solution and will be precipitated from it in the form of carbides of the specific composition upon subsequent heating (tempering).

This is also true in principle of the alpha phase, the precipitation of which it should be possible to arrest through rapid cooling of the steel. However, it has been demonstrated by experiment [789, 576, p. 157] that in the 18-8 steel, melted from pure initial materials in vacuo and containing less than 0.005% C and 0.005% N it is not possible to achieve a fully austenitic structure even after quenching from 1150°. The same was observed with

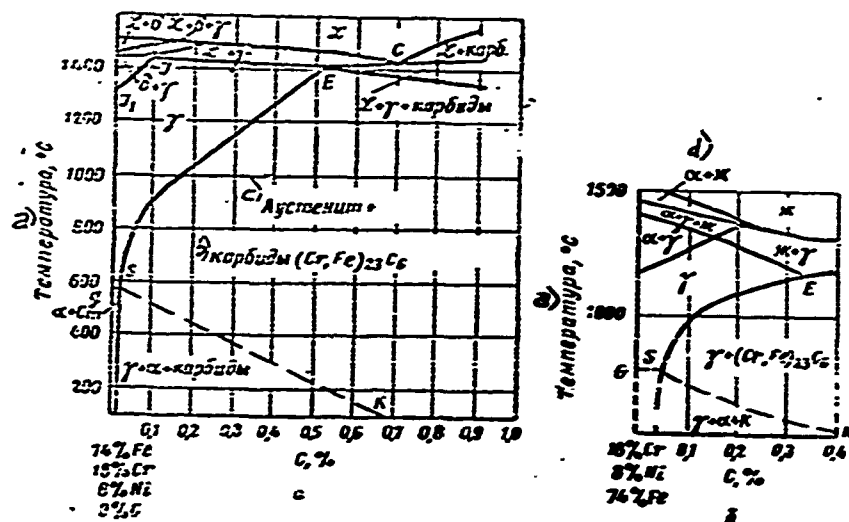


Figure 566. Pseudobinary structural diagram of Fe-Cr-Ni-C system for a section containing 18% Cr and 8% Ni.
(a) Temperature; (b) carbides; (c) austenite;
(d) alpha + iron.

18-8 steel decarburized in the solid state in vacuo to a carbon content below

0.02% [861]. Nor was a fully austenitic structure achieved after quenching from 1200° [576, p. 157] in a steel containing 0.06% C and 0.026% N but which had 0.57% Ti, which binds both the carbon and the nitrogen in the stable phases. At the same time, a fully austenitic structure is achieved after quenching from 1200° in a steel with the nitrogen content customary in industrial steels [cf. 765, 414].

Hence it is believed that steel of the 18-8 type has an austenitic structure because it always contains a certain amount of nitrogen, and such steel is additionally alloyed with titanium because of the increased content of manganese and nickel (as against 8% Ni).

The presence of the alpha phase has a varying effect on the properties of austenitic steel. The alpha phase has an adverse effect on the heat resistance and is undesirable when the steel must have a very low magnetic inductivity because of the condition of employment. The alpha phase has a favorable effect on the tendency of the steel toward intercrystalline corrosion and on the quality of a welded joint (see [Russian] pp. 617 and 618). There are conflicting opinions as to the effect of the alpha phase on the total corrosion resistance. Theoretically it is to be expected that the difference in total corrosion resistance of steel with a gamma + alpha structure and the resistance of a steel with a monophase austenitic structure should vary in different aggressive media. In reality, the alpha phase is enriched with chromium and impoverished in nickel in comparison with the gamma phase. Hence the gamma and alpha phases should be practically equivalent with respect to resistance in media in which the resistance of the steel is determined by passivating, for example in nitric acid, including boiling nitric acid. The overvoltage of hydrogen precipitation in these phases should also be approximately the same. Consequently, acceleration of the corrosion of one phase due to adjacency of the other is scarcely possible. On the other hand, upon solution in media in which chiefly the nobler potential of nickel

is manifested, such as in sulfuric acid, the resistance of the alpha phase should be lower than that of the gamma phase, and consequently that of two-phase steel should be lower than that of single-phase steel. This pattern, which has been observed experimentally [790] may apparently be considered the most correct one. A much greater negative effect of the alpha phase on resistance in sulfuric acid as compared with nitric acid was also observed in one of the most recent studies [792]. Studies where no allowance is made for, or no indication is even given¹ of, the composition of the medium in which the test of two-phase steel was conducted cannot, in our opinion, contribute to elucidation of this problem.

The presence of chromium carbides in the structure lowers the total corrosion resistance of austenitic steel, apparently for the same reason as that suggested earlier for ferritic-martensitic steels, i.e., partly because of chromium impoverishment of the basic mass and partly because of the fact that the overvoltage of the cathodic reaction in the carbide phase differs from that in the basic mass. The corrosion resistance may be increased in this case as well by transfer of the carbides to the solid solution, this being achieved in Kh18N9 steel by quenching from a temperature of 1050 to 1100°. For the Kh18N9T steel, i. e., one additionally alloyed with titanium, it has been demonstrated in recent years that in application to definite service conditions better results are yielded by quenching from a temperature of 850 to 950° or annealing at 850° with air cooling. The advantages of such heat treatment and their probable cause will be covered in greater detail during the discussion of intercrystalline corrosion and, respectively, of steel alloyed with titanium.

The high nickel content of acid-resistant austenitic steel has induced

¹For example, in the paper by D. G. Slavin. *Metallovedeniye i termicheskaya obrabotka* [Metallography and Heat Treatment], Sb. Vnitrazh [Vnitrazh Symposium], Mashgiz, 1955, p. 196.

Many investigators to seek possible complete or partial substitution of this element. It became known a relatively long time ago that the very high chemical stability of steel of the 18-8 type is due not so much to its austenitic structure per se as to the specific features of nickel austenite. Yet the efforts to ensure that the substitute metal should also have an austenitic structure have persisted, since the presence of the alpha phase, as already noted earlier, has an adverse effect on a number of other important properties, particularly the deformability. Hence, manganese, nitrogen, and to a certain extent copper have attracted and are continuing to attract the most attention as alloying elements which may replace nickel. From the diagram given earlier in Figures 346 and 335 it is to be seen that it is impossible in a steel containing over 13% Cr to achieve an austenitic structure by alloying with manganese if the carbon content is low and no nickel is present. The effectiveness of manganese when partially replacing nickel increases with reduction of the chromium content, especially below 13% (cf. Fig. 334). The achievement of an austenitic structure is greatly facilitated in all cases when the steel is alloyed with nitrogen. It may be seen by comparing Figures 334 and 335 that the introduction of even 0.15% N produces a great effect. Chromium-manganese steels with no nickel and alloyed with a very large quantity of nitrogen (up to 0.75%) have of late been, and are now being, developed in the USA, chiefly as heat-resistant steels with a stable austenitic structure. It has been found in this case that in a steel containing 17% Cr and 15% Mn, an austenitic structure can be achieved with 0.4% N, and in a steel containing 17% Cr, 13% Mn, and 2.5% Mo, with 0.75% N.

However, with respect to general corrosion resistance, chromium-manganese steels, both with and without nitrogen, are markedly inferior to chromium-nickel steel. They are especially sensitive to pitting corrosion, which is detected, for example, upon spraying with a salt solution. Alloying of chromium-manganese steels with nickel not only increases the stability of

substitute, but also increases their corrosion resistance in a number of media. As an illustration, Figure 367a [455] shows the effect of nickel on the resistance of a steel containing 16% Cr and a total $(Mn + Ni) = 8\%$ in boiling

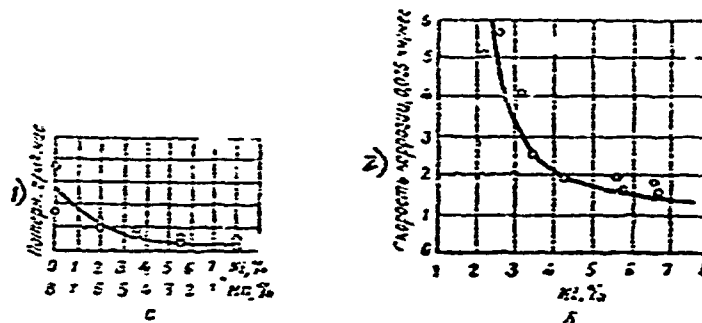


Figure 367. Effect of nickel on corrosion resistance: a - steel containing 16% Cr and a total of $Mn + Ni = 8$ in boiling 37-percent HNO_3 ; b - steel containing 17% Cr and 10% Mn in boiling 65-percent HNO_3 ; (1) loss, kg/m^2 hour; (2) corrosion rate 0.025 mm/month.

37-percent nitric acid, and Figure 367b - its effect on a steel containing 17% Cr and 10% Mn in boiling 65-percent nitric acid. In both cases the resistance increases especially sharply to approximately 4% Ni. The sensitivity to pitting corrosion is practically eliminated with a content of 5 to 6% Ni. Manganese lowers the corrosion resistance in oxidizing media, although not very greatly.

Hence the steel containing 0.1% C, 15% Cr, 15 to 16% Mn, and 1% Ni with no nitrogen or with 0.15% N, employed in the USA [696, 875] for cold-rolled sheets, bands, etc., is approximately equivalent with respect to total corrosion resistance to the semi-ferritic 17-percent chromium steel, and the chief aim in developing such steel was to achieve a maximum saving of nickel. Such, apparently, is also the purpose of similar chromium-manganese steels of the 14-8 and 15-14 type containing 0.1% C and 0.1% N, as well as of the 19-8 and 17-16 type with no nitrogen but with 0.15 to 0.20% C and containing only 1 to 1.5% Ni. These steels are being used in the German Democratic

Republic and the Federal Republic of Germany.

Various chromium-manganese and chromium-manganese-nickel steels have been developed in the Soviet Union as a result of numerous studies [see, for example, 486, 506, 493]. Of these, the one chiefly used as a corrosion-resistant steel for cold-rolled articles is the Kh13X4G9 containing 0.15 to 0.30% C and no nitrogen. This steel consequently has a well-justified composition with respect to the nickel and manganese content from the standpoint of corrosion resistance, and with respect to the chromium and carbon content from the standpoint of austenite stability. However, the corrosion resistance increases greatly with increase in the chromium content, and abroad it is chiefly chromium-manganese-nickel steels with 17 to 18% Cr and a low carbon content, and additionally alloyed with nitrogen, which are being developed. One can see from Table 102 [673] that in the USA use is even made, as an experimental steel, of a steel containing 20% Cr in which respectively the nickel and the nitrogen contents have been increased. A steel similar to the American 201 and containing on the average 17% Cr, 4.5% Ni, 6.5% Mn, and 0.12% N is also used in England [192]. The positive effect of chromium on the corrosion resistance of chromium-manganese-nickel steel in boiling 65-percent nitric acid, when the chromium content is increased from 18 to 21%, may be seen from Figure 366 [187].

The chromium-manganese-nickel steels, even those containing up to 20% Cr, are nevertheless inferior to chromium-nickel steels with respect to resistance to general corrosion. In synthetic sea water¹ at room temperature (length of test period 240 hours), a chromium-manganese-nickel steel containing 4% Ni was found to be much less resistant than a chromium-nickel steel, its resistance decreasing with increase in the carbon content, as is to be

¹Composition: per liter of water, 15.6 g NaCl, 4.28 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 2.05 g K_2SO_4 , Fe_2O_3 , 0.5 g ZnSO_4 , 0.91 g $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 0.1 g CaCO_3 .

Table 102

Chemical Composition, in %, of Certain Chromium-Manganese-Nickel Acid Resistant Steels Employed Recently in the USA

Number of steel	ASTM type	Designation	C	Mn	Cr	Ni	N
1	304	18-8	<0.15	5.5-7.5	16.0-18.0	10-12.5	0.025
2	302	18-8	<0.15	7.5-10.0	17.0-19.0	10-12.5	0.025
3	—	204	<0.10	7.5-10.0	17.0-19.0	10-12.5	0.025
4	—	344	<0.06	7.5-10.0	17.0-19.0	10-12.5	0.025
5	—	20-6-8*	<0.10	7.0-9.0	19.0-21.0	5.0-7.0	0.025-0.35

* Experimental steel.

seen from the following figures [499]:

18-8 Chromium-nickel steel		18-4-8 Chromium-manganese-nickel steel	
C, %	Average weight loss, g/m ² /hour	C, %	Average weight loss, g/m ² /hour
0.16	0.0008	0.16	0.0047
0.22	0.0005	0.26	0.0035
0.31	0.0007	0.33	0.0145

Nevertheless, the resistance of chromium-manganese-nickel steels to the action of a number of media is quite adequate, even if they are inferior to chromium-nickel steels. In certain media such as sulfuric, phosphoric, 10-percent acetic, and 20-percent lactic acid, orange and tomato juice, etc., they, just as chromium-nickel steel, are fully resistant, while in a mixture of 10-percent sulfuric and 2-percent nitric acids they are even somewhat superior to the latter. It has been demonstrated [458] that chromium-manganese steels of the 18-8 type can replace 18-8 chromium-nickel steel in the production of nitric acid by the method of ammonia contact oxidation, and that they have no especially high resistance under the conditions of cellulose production. These authors have also confirmed the fact that about 2% copper can replace a part of the nickel in chromium-manganese steel and substantially improve its corrosion resistance. They recommend a steel containing 16% Cr,

18-8, 2% Cu, and 2% Ni as one which approaches chromium-nickel steel the most closely. According to their data, such a steel behaves even better in sulfuric acid than does the chromium-nickel steel.

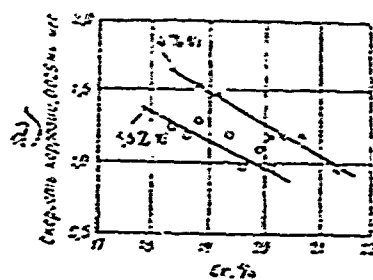


Figure 368. Effect of chromium in the 18 to 21% range on the corrosion resistance of chromium-manganese-nickel steel in boiling 65-percent HNO₃. (a) corrosion rate, 0.025 mm/month.

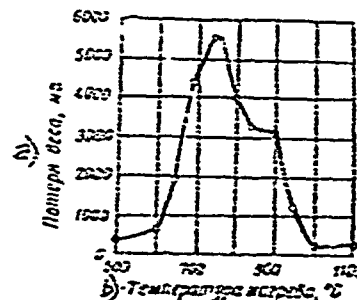


Figure 369. Corrosion resistance of 18-8 steel, containing 5.2% Mo and 0.5% Ti in 25% H₂SO₄ at 40°C versus preheating temperature. (a) weight loss, mg; (b) heating temperature, °C.

The corrosion resistance of high-chromium ferritic-martensitic, as well as chromium-nickel and chromium-manganese-nickel austenitic steels, as has been established in several studies [591, 748, 576, p. 128], drops when the sigma phase is present in their structure. It has been demonstrated in this case with a steel of the 1Kh18N9T type [576, p. 128], that the drop in resistance in boiling 65-percent nitric acid is chiefly the result of intensified corrosion of the sigma phase itself. It is true that the probability of appearance of the sigma phase is especially great in steels containing an increased amount of chromium, those of the Kh23N13 type (see Fig. 346). However, as pointed out on [Russian] p. 364, formation of the sigma phase is greatly facilitated by impurities and by many additional alloying elements. This makes possible the appearance of the sigma phase even in a steel of the 18-8 type, especially if it is additionally alloyed with molybdenum, titanium, etc. In particular, in the paper referred to [576], in which intensified corrosion of steel of the 18-8 type containing titanium due to the sigma phase

was observed, the formation of this phase was favored by insignificant quantities of aluminum and a portion of the titanium, which is converted to the solid solution upon quenching from a high temperature. Figure 369 [341] shows as an example the sharp drop in the resistance of 18-8 steel containing 3.4% Mo and 0.3% Ti in 25-percent sulfuric acid at 40° due to formation of the sigma phase upon heating in the 600 to 975° temperature range.

Increased chemical stability of steels in certain media can be achieved by additional alloying of the steels. The greatest effect is produced by molybdenum and copper. Molybdenum brings about an especially great increase in the resistance of steel in boiling nitric acid, as well as in a number of other nonorganic and organic acids and salt solutions, particularly in sulfuric acid, at elevated temperatures and in high concentrations. In Figure 370, in which are shown equal weight-loss curves based on the data of various German researchers, one can see the special advantage in this case of simultaneous introduction of molybdenum and copper into steel of the 18-8 type. Also to be seen from Figure 370 are the external conditions (temperature and concentration of the aggressive medium) under which each of these elements individually exerts a positive effect. Molybdenum also reduces the tendency of the steel to pitting [374]. In steels designed for service under severe conditions of chemical action, the molybdenum content is increased almost to 4%, and sometimes even higher. The Zr15W12N3F steel, which contains up to 4% Mo, may serve as an example. Since molybdenum contributes to formation of the alpha phase, having a far greater effect in this direction than chromium, to obtain a monophasic austenitic structure the nickel content in the steel has been increased on the average to 12%.

Numerous studies have shown that, in order to impart to steel a high stability in solutions of sulfuric acid of weak and medium concentrations, especially at the boiling point, it is necessary, in addition to alloying with molybdenum and copper, to increase the nickel content of the steel to

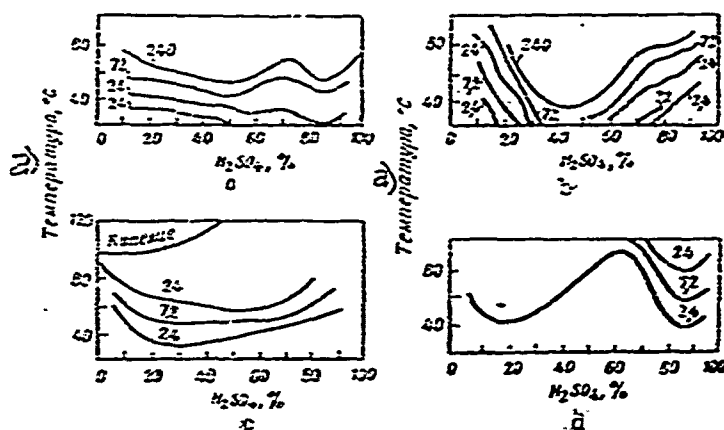


Figure 370. Effect of additional alloying with molybdenum and copper on the resistance of 18-8 steel in sulfuric acid at various temperatures:
 a - 18-8; b - 18-8 + Mo; c - 18-8 + Cu; d - 18-8 + Mo + Cu. The figures on the curves indicate losses in g/m^2 per twenty-four hours.
 (a) temperature, °C.

quantities greater than those required for obtaining stable austenite. The comparison of the stability of various steels in sulfuric acid at the boiling point, as shown in Figure 371 [869], indicates that a very great effect is achieved even upon transition from 18-12-3-2 to 8-18-3-2 steel (the third figure is the molybdenum content and the fourth that of copper). The latter is close in composition to the steel proposed by Yu. A. Kakhendzi [876]. But steels containing over 25% Ni have an even higher stability under these conditions. This corresponds roughly to a concentration of 2/8 mole nickel, at which, according to Figure 359, the nickel exerts its greatest positive effect on the stability of steel in sulfuric acid.

The principle of simultaneous alloying with nickel in an amount now lower than 2/8 mole, molybdenum in the amount of 2 to 4%, and 3 to 4% copper is the basis of the steels developed in recent years at home and abroad which possess the highest resistance in solutions of sulfuric acid in high concentrations and at elevated temperatures. Examples of such steels, in which

the differences in composition are, on the whole, no longer fundamental, are given in Table 103. All these steels are stable toward pitting, but are prone, especially under certain welding conditions, to intercrystalline corrosion. The sensitivity to intercrystalline corrosion is eliminated upon introduction of titanium or niobium into the steel. The Kh25Kh27A2F and 20S steels may be cited as examples. The latter is a version of the American 20 steel, into which niobium (Columbium, Co) is introduced. The Kh25Kh28Kh3D3 (21629) steel possesses high resistance to intercrystalline corrosion. As regards their resistance to

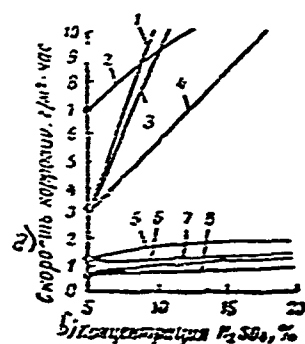


Figure 571. Corrosion of variously alloyed steels in sulfuric acid of varying concentration at the boiling point. Length of test period 100 hours:

- 1 - Kh18N9T; 2 - 8-18; 3 - 18-12-3;
- 4 - 18-12-3-2; 5 - 8-18-3-2;
- 6 - 18-18-6-2; 7 - 18-25-3-2;
- 8 - 18-28-3; 20-28-3-3, and 18-25-4-2;

(a) corrosion rate g/m^2 /hour;
(b) concentration of H_2SO_4 , %.

general corrosion resistance is illustrated by the curves of Figure 571 for a concentration of up to 20% at the boiling point. Steel 1 (Table 103) at concentrations of up to about 30% and a temperature of up to 60° may be characterized as resistant (weight losses 0.01 to $0.1 g/m^2$ /hour) or very resistant (losses from 0.001 to $0.01 g/m^2$ /hour, and at higher temperatures as having lower resistance (losses from 0.1 to $1 g/m^2$ /hour) [see 875, Table 5]. Data are cited [862] for the American steel (3 in Table 103) from which it is to be seen that with respect to the resistance in 10-percent sulfuric acid at the boiling point it is approximately 10 times superior to steel of the 18-12-3 type (and even more so in higher concentrations

and at lower temperatures). In Germany, however, it is felt [see 770] that only in rare instances does its greater resistance justify its higher cost, in comparison with the 18-18-2-2 steel employed there.

Table 105.

Chemical Composition (average), %, of Austenitic Steels Possessing High Resistance in Sulfuric Acid Solutions in High Concentrations and at Elevated Temperatures.

Number of Steel	C	Cr	Ni	Mo	Cu	Country	Designation	Source
1	up to 0.1	25	25	5	5	USSR	Kh25N25Mo5 (SI555)	[875]
2	up to 0.1	18	28	5	5		Kh18N28Mo5Ds	[868]
3	up to 0.07	20	25	2	3	USA	20	[862, 877]
4*	up to 0.07	20	26	2.5	4		CX-7K	[872]

* Cast steel.

Further increase in the resistance in hot sulfuric acid is achieved by increasing the nickel content to about 3/3 mole. As an example we may cite a steel containing on the average 0.05% C, 0.4% Si, 0.6% Mn, 21% Cr, 40% Ni, 3% Mo, and 1.75% Cu, which is stable in hot sulfuric, nitric, and phosphoric acids, in boiling concentrated acetic acid, etc. [894]. It is true that such steel already contains more nickel than iron, and has accordingly been termed "nicel". It may be considered as transitional to the nickel-based alloys.

The positive effect of copper and molybdenum on the chemical stability of steel in certain media is related to their solution in the basic mass and according to A. I. Shultin [417] can be explained on the basis of the principle of "secondary electrochemical exchange". If the steel is alloyed with copper or molybdenum, at the points of defects in the passivating film, ions of the copper or molybdenum also pass into solution simultaneously with the ions of the base metal, i.e., the crystal lattice is entirely destroyed. The corrosion process may subsequently proceed "in exchange" both for the hydrogen

ions and for the ions of these metals. The latter, being reduced, stop up the pores in the passivating film, provided, of course, that these pores are small. This hypothesis has indeed received some experimental confirmation in special tests, in which the molybdenum ions were contained in the attacking acid [46].

In suggesting the same mechanism of accumulation of alloying elements on the surface of steel, N. B. Tomashov and others (see [Russian] p. 597) ascribe the positive effect of copper, as well as of other "cathodic admixtures", to the fact that they contribute to stronger anodic polarization of the basic anode background in the structure of the steel, and by virtue of this facilitate the transition of the latter into a stable passive state. Note that in discussing this question on [Russian] page 597, we also suggested the possibility of a different explanation of the positive role of the effect of noble alloying elements, on the basis of the purely "solution-type" mechanism of their action.

Even more greatly resistant in various highly aggressive media than the high-alloy austenitic steels containing molybdenum and copper are the nickel-based alloys, primarily nickel-molybdenum or nickel-chromium-molybdenum alloys--the Hastelloys. The chemical composition of such alloys, which are employed as heat-resistant ones, is given in Table 96. Certain varieties of these alloys are also used in the chemical industry as acid-resistant ones, as is to be seen from Table 104 [see 770]. Alloy 4 was developed in recent years and is the most economical one, approaching the high-alloy steels, particularly Monel, in composition. Alloy 1 is little used, alloys 2 and 3 are being put to the widest use. Alloy 2 (roughly Hastelloy B) is relatively resistant to hydrochloric and sulfuric acids of any concentrations at elevated temperatures, up to the boiling point. Alloy 3 (approaching Hastelloy C) possesses a high resistance to nitric acid, chlorides, etc. With respect to stability in hydrochloric acid it is inferior to alloy 2, but does not react to the presence of

oxidizers. The stability of alloy 2 in hydrochloric acid, on the other hand, drops sharply upon the addition of oxidizers. Nevertheless, under certain less severe conditions high-alloyed austenitic steel containing molybdenum and copper is not too inferior to the Hastelloys in chemical stability, as may be seen from data given later [877, Table 14] on the corrosion of the several steels and alloys in 78-percent sulfuric acid upon addition to the latter of sulfonation products.

Table 104

Chemical Composition and Mechanical Properties of Acid-Resistant
Nickel-based Alloys

No. of alloy	Chemical composition (av) %						Mechanical properties			
	C	Cr	Mo	Ni	Fe	Ti+Nb	σ_s kg/mm ²	σ_b kg/mm ²	δ (1-5%)	ψ
1	<0.10	—	21	58	19	—	39	75	50	45
2	<0.10	—	28	65	5.5	—	42	95	50	45
3	<0.10	15.5	17	60	5.5	—	38	90	35	40
4	<0.10	22	6.5	46	22	2.2	35	75	50	45

	Corrosion, 0.001 inch/year	
	at 27°	at 60°
Steel 316 (16-18% Cr, 10-14% Ni, 2-3% Mo)	0.2	20.0
Hastelloy B	—	0.6
Hastelloy C	—	1.5
Steel 20 (3 in Table 105)	None	5.0
Nikonel	None	8.0

It must be borne in mind that, especially in welding or service at an elevated temperature, these alloys, as may be seen from Figure 372 [779], tend toward precipitation hardening (Fig. 372a) due to the metallic fusion of the nickel with molybdenum, this being accompanied by decrease in their acid resistance (Fig. 372b). Heating at 1050 to 1075° for alloy 2 and at 1125° for alloy 3 plus air cooling is recommended as "stabilizing" treatment.

The high chemical resistance of Hastelloy B is apparently determined by the resistance of the molybdenum. Hence study is being devoted at the present time to the possibility of employing pure molybdenum for the manufacture of certain components of chemical equipment which functions under especially aggressive conditions [see 893].

Steels containing a reduced amount of nickel and in point of their structure occupying a position intermediate between the austenitic and ferritic or semi-ferritic steels have been developed in recent years and already put to practical use to a certain extent. In order to increase their resistance in dilute sulfuric acid, such steels are generally additionally alloyed with molybdenum. Such, for example, are steels containing 17% Cr, 4% Ni, and 4% Cu [809, 892], those with 17% Cr, 4.2% Ni, and 2.75% Mo [678], and high-chromium steel containing nickel and molybdenum. Concerning the first two, see [Russian] p. 535. The third steel is employed in the USA under the designation 329, i.e., it is classified as an austenitic steel of the 300 series, and not a ferritic-martensitic one of the 400 series, because of its higher nickel content [817]. The composition of this steel is up to 0.1% C, 23 to 26% Cr, 3 to 5% Ni, and 1 to 2% Mo. Its structure at room temperature in the annealed state consists of ferrite, carbides, and 20 to 40% stable austenite, which is formed upon cooling.

According to available information [879], the 329 steel is not inferior in resistance to general corrosion in nitric acid to steel of the 18-8 type, and excels the latter in resistance in sulfuric acid, chiefly because of the molybdenum it contains. At 40° in the annealed state, it possesses the same resistance in 10-percent sulfuric acid as does chromium-nickel-molybdenum steel of the 18-12-3 type. Holding in the 600 to 850° range leads to formation of the sigma phase, and this may be utilized to strengthen the steel by precipitation hardening (see [Russian] p. 629 and Fig. 382). But its corrosion resistance decreases appreciably in this case. This steel is used in

Sweden in particular is beginning to be used in other countries as a fairly resistant one in the production of acetic acid.

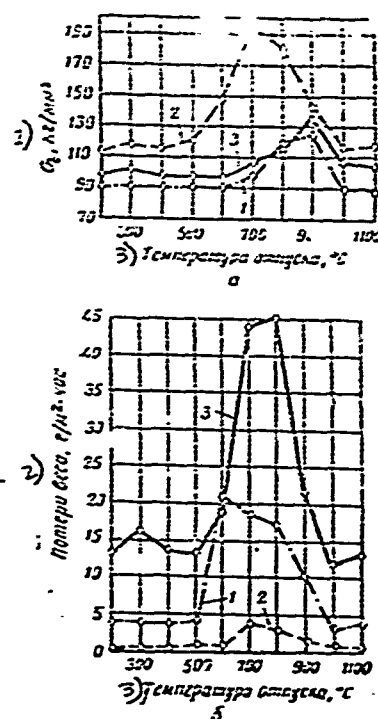


Figure 372. Effect of tempering (for 25 hours; however, the effect is also observed with shorter holding) after quenching on the ultimate strength (a) and resistance in boiling 10-percent hydrochloric acid (b) of alloys based on nickel (composition and properties indicated in Table 104). Quenching conditions: 1 - 1175°, 15 min., water; 2 - same; 3 - 1190°, 15 min., water;

(1) σ_b , kg/mm², (2) weight losses, g/cm²/hour; (3) tempering temperature, °C.

B. INTERCRYSTALLINE CORROSION OF STAINLESS AND ACID RESISTANT STEELS

Principal phenomena and factual data

Intercrystalline corrosion is one of the most dangerous forms of corrosion, since it leads to weakening of the bond between the grains of the steel and to a sharp drop in its plasticity and ductility. Although many methods of establishing the tendency of steel toward intercrystalline corrosion have been standardized in various countries, the problem of a reliable procedure is far from solved and is undergoing discussion [860]. From the standpoint of the nature of the phenomenon, it is important to note that in a number of cases steel is found to be resistant to intercrystalline corrosion in one aggressive medium and not resistant or less resistant in another.

Austenitic chromium-nickel, chromium-manganese, and chromium-manganese-

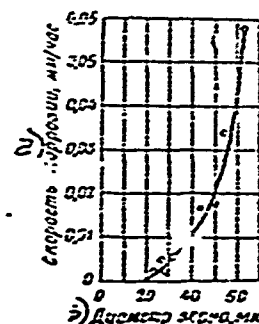
nickel steels and high-chromium ferritic and semi-ferritic steels containing 16 to 28% Cr are subject to intercrystalline corrosion. However, the heat treatment conditions which cause and eliminate the tendency toward intercrystalline corrosion differ for austenitic and ferritic steels.

Ferritic steels [see 794, 881] become sensitive to intercrystalline corrosion only after rapid cooling, for example in water or air, from a temperature above 900 to 925°. After slow cooling from the same temperatures, the steels do not have this defect. It has been shown [793] that after very rapid cooling as well, the steels are not prone to intercrystalline corrosion. To rectify the condition of ferritic steel which has become sensitive to intercrystalline corrosion, it is sufficient to heat it for 3 to 5 minutes at a temperature of 650 to 800°.

Characteristic of ferritic steels is the very slight dependence of their tendency toward intercrystalline corrosion on the carbon content. Steels containing only about 0.01% C [792] and even 0.005% C have also been found to be sensitive, if the quantity of nitrogen in them is greater than 0.01% [802]. With a high chromium content, fluctuations over the 0.03 to 0.12% C range have little effect. According to certain data [794, discussion in 792], the effect of chromium is manifested in the circumstance that with increase in its content there occurs a rise in the heating temperature, a drastic quench which imparts to steel a tendency toward intercrystalline corrosion. According to other data [793], chromium has no effect on this temperature. The divergence is probably to be ascribed to the different percentages of carbon, nitrogen, and impurities in the steels studied by different authors. Chromium should exert a greater effect on the "critical" temperature at a higher percentage of carbon, nitrogen, etc., inasmuch as solution of the chromium phases apparently occurs upon heating. The rate of intercrystalline corrosion increases sharply with coarsening of the grain, as may be seen from Figure 373 [794] for a steel with 0.044% C and 25% Cr.

Figure 373. Rate of intercrystalline corrosion (in a solution of phosphoric acid with copper sulfate) of high-chromium steel containing 25% Cr and 0.044% C versus grain size.

- (a) corrosion rate, mm/hour;
(b) grain diameter, μ .



In contrast to the ferritic steels, austenitic steel of the Kh18K9 type is not prone to intercrystalline corrosion after quenching from 1050 to 1100° and acquires this tendency as a result of subsequent heating (tempering) over the 450 to 850° range. The sensitivity to intercrystalline corrosion acquired by a steel as a result of heating in the temperature range indicated, is highly dependent on the length of the heating period and passes through a maximum. The kinetics of development of the processes imparting to steel a tendency toward intercrystalline corrosion and immunity to it, versus the heating temperature, is shown in Figure 374a [790] and in Figure 374b [681]. Curve 1

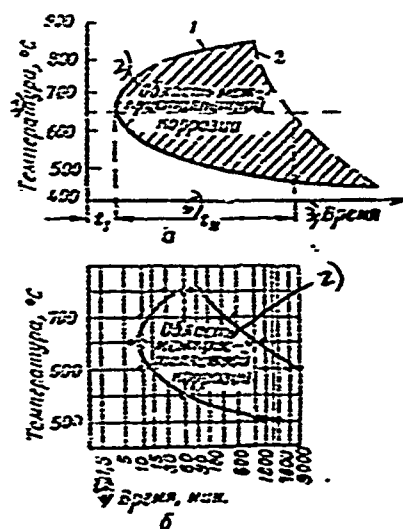


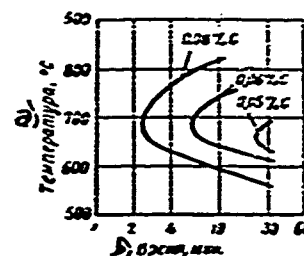
Figure 374. Effect of heating (tempering) temperature and length of holding period on the development of processes causing intercrystalline corrosion in austenitic steel:
a - schematic; b - Kh20Kh14S2;
(1) temperature, °C; (2) region of intercrystalline corrosion;
(3) time; (4) time, minutes;
(5) t_i

denotes the time t_1 during which the steel has not yet acquired the tendency toward intercrystalline corrosion, and curve 2 the time t_2 after which it acquires immunity to it. The time t_1 decreases up to around 650° and then increases again, while the time t_2 is the shorter, the higher is the temperature.

Another difference between austenitic and ferritic steels lies in the circumstance that carbon in an amount exceeding the limit of its solubility at room temperature sharply increases their tendency toward intercrystalline corrosion. This is illustrated by the kinetic curves for 18-8 steel in Figure 375 [800], from which it may be seen that with 0.08% C intercrystalline corrosion appears after heating for 3 minutes at 600° ; with 0.06% C after 8 minutes at 650° ; and with 0.05% C after 25 minutes at 640° . Steel with 0.03% C did not acquire the tendency toward intercrystalline corrosion even after heating for 50 hours at 640° . Nevertheless, this steel is sensitive to intercrystalline corrosion in individual cases when it contains a very small amount of carbon (particularly, about 0.003% and approximately 18% Cr and 24% Ni).

Figure 375. Kinetic curves of processes causing sensitivity to intercrystalline corrosion, for a steel of the 18-8 type containing different amounts of carbon.

(a) temperature, $^\circ\text{C}$. (b) time, minutes



The chemical composition of the austenite matrix also has an appreciable effect. Chromium-manganese steels are less prone to intercrystalline corrosion than are chromium-manganese-nickel steels, and the latter to a lesser extent than chromium-nickel of the 18-8 type [488]. The superiority of chromium-manganese-nickel steels is especially noticeable in the event of a relatively short exposure to the dangerous temperature range. An important quality of these steels also consists in the fact that they are virtually

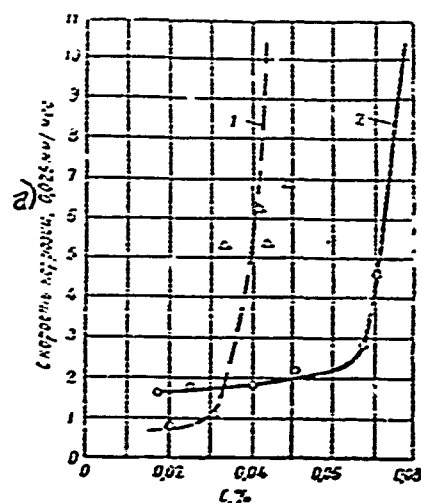


Figure 376. Effect of carbon content on tendency toward intercrystalline corrosion of chromium-nickel and chromium-manganese-nickel steel:

1 - steel containing 18 to 20% Cr and 8 to 11% Ni; 2 - steel containing 17 to 19% Cr, 4 to 6% Ni, 7.5 to 10% Mn, and up to 0.25% N (steels 202 and 204, Table 102);
(a) corrosion rate, 0.025 mm/month.

insensitive to intercrystalline corrosion up to a higher carbon content than are the chromium-nickel steels, specifically to around 0.06% C, as is to be seen from Figure 376 [673]. Despite the lack of systematic studies on the effect of the quantity of nickel itself, there are certain grounds for believing that as its percentage rises the tendency of the steel toward intercrystalline corrosion is intensified somewhat, other conditions being equal.

The tendency of austenitic steel to intercrystalline corrosion is affected by other factors besides the chemical composition. A powerful negative effect, as with ferritic steel, is exerted by coarsening of the grain, and, accordingly, by a rise of the quenching temperature above the optimum [see 305, 799]. The factors exerting a positive effect include presence of the alpha phase in the structure. The information on the effect of the sigma phase is contradictory. According to some sets of data, it contributes to intercrystalline corrosion in the event of precipitation of grains along the boundaries, while in other studies it has not been found to have a harmful effect. Considering the diversity of the factors which can affect the resistance of steel to intercrystalline corrosion, this disagreement may pro-

visionally be ascribed to a difference in conditions and in the material studied in various investigations. In particular, certain foreign research-

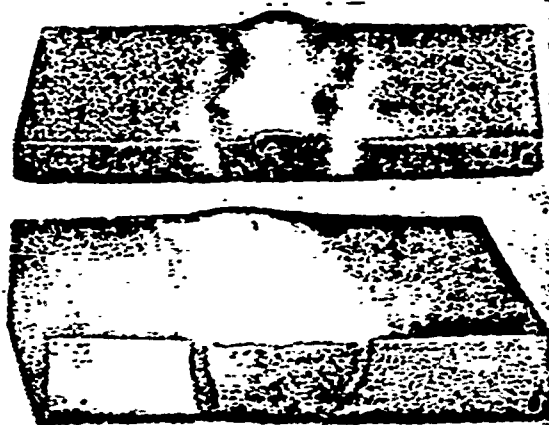


Figure 377. Intercrystalline corrosion (in a solution of 10-percent HNO_3 and 3-percent HF) of welded joints:

- a - steel containing 18 to 20% Cr and 8 to 11% Ni;
- b - steel containing 17% Cr.

ers believe that intercrystalline corrosion due to precipitation of the sigma phase on the grain boundaries manifests itself only in a boiling 65-percent solution of nitric acid. Plastic deformation exerts a substantial positive effect on the resistance of steel to intercrystalline corrosion.

The tendency of steel to intercrystalline corrosion is of great importance for articles in service in the temperature range which is dangerous from the standpoint of this phenomenon, but of even greater importance for articles which are subjected to welding. One of the features of high-chromium ferritic steels lies in the fact that welded joints produced from them are not attacked by intercrystalline corrosion at a certain distance from the joint but in the zone immediately adjacent to it, which may be seen from the illustration in Figure 377 [193]. This is apparently explained by the fact that ferritic steels are subject to intercrystalline corrosion only after heating to temperatures above 900 to 925°. However, this effect, for reasons not yet clear, is sometimes observed [190] in welded joints of austenitic steels.

has sufficient study as yet been devoted to the concentration occasionally observed in austenitic steels of general corrosion in a narrow zone on the boundary between the joint and the base metal, it having been named "knife-like" or "thread-like" corrosion in the foreign literature (knife-line attack, Messerschnittkorrosion).

Elimination or substantial reduction of the tendency of austenitic steel to intercrystalline corrosion is possible in principle by several methods. The first method consists in lowering the carbon content of the steel to the limit of its solubility at room temperature, i.e., to 0.02 to 0.03%. Such steels, which were previously melted in small quantities only in induction furnaces, particularly in vacuo, from the wastage of chromium-nickel steel [897]¹, have in recent years been melted in large electric arc furnaces and poured into ingots weighing up to 7 tons [773, 795].

This is achieved by blowing oxygen through the bath, the employment, in the form of fine granules (this accelerating solution 2 to 3-fold), of special ferrochromium containing no more than 0.02% C, about 5% Si, approximately 65% Cr and a certain amount of silica, 99-percent electrolytic ferromanganese, and careful regulation of the pouring temperature. Additional weakening of intercrystalline corrosion is achieved by brief heating of the welded joint of this steel with the aim of relieving the residual stresses.

Certain acid-resistant steel with a very low carbon content have already been standardized. We may give as examples the American steels 304L containing 18 to 20% Cr and 8 to 12% Ni and the 326L containing 16 to 18% Cr, 10 to 14% Ni, and 2 to 3% Mo, which differ from the similar steels 304 and 316 only in that they contain no more than 0.03% C. Among the chromium-manganese-nickel steels, such a one is the 204L steel cited in Table 102, which differs from steel 204 only in its content of $\leq 0.06\%$ C. Studies show [800] that

¹In the report by E. S. Belyakov.

chromium-nickel steel containing $< 0.05\%$ C is required if sheets over 20 to 25 mm in thickness are to be subjected to welding without subsequent quenching. A steel containing up to 0.05% C is suitable for sheets of lesser thickness. The disadvantages of "super-low-carbon" steel include the higher cost of the latter and the 475-degree brittleness (see [Russian] p. 546) inherent in high-chromium steels. Its additional merits include a higher resistance to general corrosion as well.

The second method consists in producing a considerable amount of the alpha phase in the structure of the steel. Highly effective use may be made of partial ferritization of the structure with the aim of increasing the resistance to intercrystalline corrosion in welded joints [790]. To obtain an austenitic-ferritic welded joint, new electrodes have been developed [790] which contain an increased amount of ferritizing elements, particularly up to 22% Cr and up to 2.8% Si, as well as vanadium. As has been demonstrated by experiment, vanadium acts in this case not so much as a carbide-forming element but as a ferritizing element.

The third, most widespread, method of eliminating or reducing the tendency of steel to intercrystalline corrosion consists of additional alloying of it with titanium or niobium (Nb + Ti). It has also been demonstrated [800] that molybdenum produces a positive, although less perceptible, effect. The basic aim of introducing these elements is to bind the carbon contained in the steel in stable carbides which, in contrast to chromium carbides, should not dissolve at the quenching temperature, owing to which fact their precipitation along the grain boundaries upon subsequent heating is prevented. Hence the amount of titanium or niobium introduced usually corresponds to the stoichiometric ratio for their carbides; specifically, that of titanium is no lower than 5 (C -- 0.005) and that of niobium no lower than 8 (C -- 0.05).

Despite the fact that properties which are better in some respects have been established for steel of the Kh18N9 type, which is alloyed with niobium

[see 796], steels additionally alloyed with titanium have been put to the widest industrial use as chemically stable steels for welded joints and structures. However, titanium becomes very strongly oxidized in welded joints with no protective medium present. Hence welded joints are usually alloyed with niobium, even when the steel itself is alloyed with titanium rather than niobium. But since niobium, when contained in the joint in amounts up to 1%, contributes to the formation of hot cracks [see 790], the possibility referred to above of immunizing welded joints to intercrystalline corrosion by alloying them with ferritizing elements acquires special importance.

Of the steels alloyed with titanium the most widely used is that of the 12Kh16N9T type. The heat treatment adopted for it, consisting in quenching from 1050 to 1100°, is designed to combine high plasticity and toughness with high corrosion resistance.

Instances, however, have been registered when even steel alloyed with titanium is subject to intercrystalline corrosion. The opinion [e.g., 797], confirmed by experiment, has been advanced that the amount of titanium determined from the stoichiometric ratio for its carbide is inadequate, since not all the titanium is bound by carbon, and a portion of it is to be found in the solid solution, oxides, and nitrides. But such phenomena are observed even in steels in which the quantity of titanium is far in excess of the stoichiometric proportion. Hence special attention has been devoted in recent years to the conditions of heat treatment of steels alloyed with titanium, and it has been recommended [799, 801, 576, p. 125] that, in place of quenching from the conventional temperatures of 1050 to 1100°, it be subjected to stabilizing treatment from 850 to 900° (or somewhat higher) accompanied by water or air cooling, if especially high plasticity and ductility values are required of the steel.

The significance of stabilizing treatment lies in the fact that at high temperatures a part of the titanium carbides passes into the solid solution.

It is to be seen from Figure 373 [799], that the solution of titanium carbides begins at approximately 900°. When the steel is quenched above 900°, the solid solution, which is supersaturated with carbon and contains two alloying carbide-forming elements, becomes, consequently, fixed. From consideration of the thermodynamic and kinetic factors governing the decomposition of such a supersaturated solid solution (see [Russian] p. 174) it follows that at relatively low temperature (for the given system), chromium carbide must be precipitated. A rise in tempering temperature must cause the separation of a mixture of chromium and titanium carbides, to be followed by precipitation of titanium carbide. In fact, it has been established experimentally [798] for a steel of the 18-8 type containing 0.07% C and 0.4% Ti and quenched from 900 to 1500°, that principally chromium carbide and only a small amount of titanium carbide are precipitated upon subsequent heating at 600°. At 700°, the carbides of chromium and titanium are precipitated simultaneously, and at 800° the amount of chromium carbides decreases and that of titanium carbides increases.

Consequently, the stabilizing treatment at 850 to 900° consists essentially in the fact that after such treatment only titanium carbides should be present in the basic mass of austenite, whereupon the steel should not be prone to intercrystalline corrosion after heating in the dangerous temperature range. The resistance to general corrosion in certain media, particularly boiling nitric acid, as may be seen from Table 105, drops only slightly after stabilizing treatment as compared with quenching from 1100°, while it increases several times if the steel is subjected to additional tempering at 650°. This is an additional highly important advantage of the stability treatment over conventional treatment (quenching from 1050 to 1100°).

We shall note in passing that the increase in the solubility with lowering of the quenching temperature justifies the conclusion that titanium carbides lower the general corrosion resistance of steel, although more faintly

than chromium carbides. On the other hand, it follows from the fact of a sharp increase in solubility after additional tempering at 650° (if the steel is quenched from temperatures above 900°), that the presence of a mixture of chromium and titanium carbides in a definite quantitative ratio has the most harmful effect.

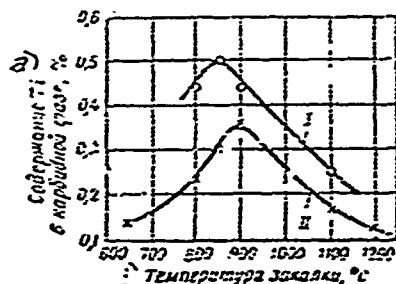
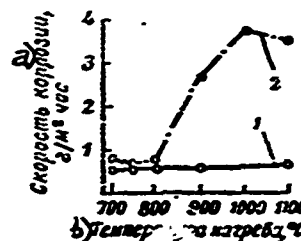


Figure 378. Titanium content in the carbide phase of 1Kh16N9T steel as a function of the quenching temperature (melts I and II).
(a) Ti content of carbide phase, %; (b) quenching temperature, $^{\circ}\text{C}$.

Additional alloying with titanium is also the principal means of lowering the tendency toward intercrystalline corrosion for ferritic and semi-ferritic chromium steels. An example is given for 17-percent chromium steel in Figure 379 [881]. The data are conflicting as regards the effect of niobium. The data also disagree as to the quantity of titanium which must be

Figure 379. Effect of additional alloying with titanium on intercrystalline corrosion of Kh17 steel in boiling 60-percent nitric acid:
1 - Kh17 steel with no titanium;
2 - Kh17 steel containing titanium;
(a) corrosion rate, $\text{g}/\text{cm}^2/\text{hour}$;
(b) heating temperature, $^{\circ}\text{C}$.



introduced into steel in order to prevent intercrystalline corrosion. Since in ferritic steels carbon exerts an effect even when contained in very small percentages, apparently because of its negligible solubility in ferrite at room temperature, the amount of titanium must be sufficient to bind all the carbon. Moreover, there is justification for assuming (see [Russian] p. 627) that the responsibility for the tendency of ferritic steels to intercrystalline corrosion is borne not only (and possibly not so much) by the carbides, but

also by the nitrides, which are precipitated along the grain boundaries. Consequently, titanium should also bind the nitrogen in stable nitrides. It is thus to be expected that the minimum amount of titanium should be greater than in austenitic steel.

It is possible that the "normal" nitrogen content of steel -- not always taken into account -- is one of the reasons for the disagreement of the data on the necessary amount of titanium. Also of great importance in the composition of the medium in which the test is conducted. Thus, according to certain sets of data [803], which pertain to a steel containing 17% Cr, in

Table 105.

Effect of Conditions of Heat Treatment of 1Kh18N9T Steel on weight loss¹
 $\text{g/m}^2/\text{hour}$, in Boiling Nitric Acid

Heating temperature, °C						
1100	1000	950	900	850	800	Source
Water cooling						
$\frac{0.97}{10.1}$	$\frac{1.0}{6.8}$	$\frac{1.0}{2.9}$	$\frac{1.1}{2.3}$	$\frac{1.1}{2.3}$	$\frac{1.3}{2.3}$	[801] ²
$\frac{0.256}{13,300}$	-	-	$\frac{0.262}{0.410}$	$\frac{0.290}{0.462}$	-	[799] ³
Air cooling						
-	-	-	$\frac{0.290}{0.455}$	$\frac{0.332}{0.368}$	-	[799] ³

¹The numerator denotes no additional tempering, the denominator indicates additional tempering for two hours at 650°.

²144 hours in 65-percent acid.

³100 hours in 60-percent acid.

order to eliminate the tendency toward intercrystalline corrosion in a 10-percent solution of sulfuric acid and copper sulfate, it is sufficient for the Ti:C ratio to be somewhat greater than 5:1. According to other data [802], this ratio should be greater than 6:1; and according to a third set of data [793], greater than 8:1. Yet, in boiling 65-percent nitric acid the steel is

sensitive to intercrystalline corrosion even with a Ti:C ratio greater than 17.1. It is important, moreover, to note [795] that titanium does not at all entirely eliminate the tendency of ferritic steels to intercrystalline corrosion, but merely elevates considerably the lower heating temperature after rapid cooling from which the steel acquires this tendency.

In connection with the highly probable assumption referred to above that in ferritic steels the nitrides precipitated along the grain boundaries are also responsible for intercrystalline corrosion, it is to be expected that other elements than titanium which form stable nitrides must also reduce the tendency of ferritic steels toward intercrystalline corrosion. Such an effect may be assumed, for example, in the case of their additional alloying with aluminum.

Assumptions as to the nature of intercrystalline corrosion

The nature of the processes causing and eliminating intercrystalline corrosion are highly complex and are still far from being fully ascertained. With respect to austenitic steel, the hitherto most widely accepted theory ascribes intercrystalline corrosion to precipitation of chromium carbides along the grain boundaries. This leads to impoverishment of the solid solution in this element around the carbides in the peripheral sections of the grains. Reduction of the amount of chromium in the solid solution below the limit of chemical stability according to the $n/8$ mole law, on the other hand, causes destruction of the peripheral grain layers. From the standpoint of this theory, the kinetic curve of Figure 374 reflects the rate of two processes: precipitation of the carbides and diffusion of chromium from the internal zones of the grain toward its periphery. In the case of tempering at up to 650° , the rate of chromium diffusion is still low, and there is a greater manifestation of increase in the rate of carbide precipitation. At tempering temperatures above 650° , the diffusion of chromium from the internal zones of the grain compensates at an increasingly more rapid pace the loss of this

total in the peripheral zone. Curve 2 in Figure 374 corresponds to the time during which total compensation for the loss of chromium in the peripheral zone of the grain ensues as a result of its diffusion. The role of titanium or niobium amounts to the following: in binding the carbon they prevent chromium impoverishment of the peripheral zone of the grain. There are studies [304 and others] in which the negative role of chromium depletion of the grain periphery is substantiated electrochemically, from the positions of the theory of microelements.

Hypotheses have been advanced which are "variants" of the impoverishment theory. The authors of these hypotheses hold [see 790] that the cause of intercrystalline corrosion is chromium impoverishment of the peripheral zone of the austenite grain, but that this is caused by the precipitation not of chromium carbides, but of secondary chromium ferrite or chromium nitride or several phases, which may constitute carbides, ferrite, and some other components.

However, despite the logic and external simplicity of the chromium impoverishment theory, it is doubted by certain researchers. Experimental facts have also been observed which do not lend themselves to explanation from the standpoint of this theory [882]. Some believe [41] that the stresses created by the carbides precipitated on the grain boundaries alone are sufficient to cause intercrystalline corrosion. However, if the decisive role is assigned to the stresses, it is difficult to explain the shape of the kinetic curves in Figure 374. On the other hand, it would be possible in this case to rectify the condition of a steel which has become sensitive to intercrystalline corrosion by brief heating at 750 to 800°, which is sufficient for relaxation of stresses even in austenitic steel. Others suggest that it is not the peripheral layer of the grain which is dissolved, but the precipitating phase itself, which may function as an anode in the resulting electrochemical system, particularly because it is an intermediate non-equilibrium phase [880]¹.

¹Article by I. I. Levin.

We also believe that chromium impoverishment of the peripheral layer of the grains is scarcely the probable cause of intercrystalline corrosion. In fact, chromium steels containing 13% Cr are not prone to intercrystalline corrosion either after rapid cooling from high temperatures [794, 881] or after quenching and tempering, although chromium impoverishment of the periphery of the grains should undoubtedly lead to reduction of its quantity to values below the boundary of chemical stability. On the other hand, steels with a high chromium content, such as the steel 25-20 are no less subject to intercrystalline corrosion than the 18-8, despite the fact that chromium impoverishment of the periphery of the grains to limits below the boundary of chemical stability is scarcely probable in this case. Moreover, the boundary layer of the grain (intercrystalline layer), as was stated in detail in the preceding chapters, has a semi-ordered structure and increased free energy. For this reason it must be considerably enriched, particularly in chromium, in comparison with the grain itself. It is precisely for this reason that the formation in this layer of a new phase, including the carbides, is facilitated, upon decomposition of the solid solution. Thus, chromium impoverishment upon precipitation of carbides may play a prominent part in the grain (especially so in steel in which the chromium content is near the first boundary of chemical stability) but a very slight part in the boundary layer of the grain.

In our hypothesis of the nature of intercrystalline corrosion of austenitic steel, we proceed from the premises set forth on [Russian] p. 173 (see also Fig. 103). It follows from them that in consequence of the role of the kinetic factor at relatively low tempering temperatures, metastable carbide should be precipitated, although this does not lead to the maximum, but only to a relative, change in the free energy of the system. In high-chromium steel chromium carbide $(Cr, Fe)_{23}C_6$, which is highly enriched with iron, may constitute such a carbide. With elevation of the tempering temperature, the precipitating carbide comes increasingly closer to the stable $Cr_{23}C_6$. Pro-

longer holding at the tempering temperature also leads to establishment of thermodynamic balance, i.e., to a gradual chromium enrichment of the carbide to the stable composition Cr_{23}C_6 , the time necessary for this being the shorter, the higher is the tempering temperature.

It is apparent that a change in the composition of the carbide precipitated along the grain boundary with varying temperature and time of tempering, will also lead to a change in the kinetics of electrochemical dissolution of the system, which consists of the carbide and the solid solution contiguous to it. Explanatory schematic polarization curves are given in Figure 360a, where φ_1 is the equilibrium potential of the solid solution; φ_2 is the more negative equilibrium potential of the chromium carbide, highly enriched with iron; 1 and 2 are the lines of the anode currents on each of these phases; 3 denotes the overvoltage of the reduction reaction on the carbide phase; 4, that on the solid solution; and 5 the total reduction rate on both phases. The grain boundaries of the solid solution before precipitation of the carbide phase in them are dissolved at the steady potential φ_{s1} at a low rate which is proportional to the currents $i_1 = i_2$. The carbide phase which has been precipitated would dissolve independently at a rate proportional to $i_7 = i_8$. Being present in the boundary layer of the grain, however, it is dissolved at the steady potential φ_{s2} , at the rate $i_3 = i_4$, i.e., the solid solution sharply accelerates its solution catalytically, and the steel is subjected to intense intercrystalline corrosion. But the equilibrium potential of the metastable carbide phase may also differ less from the equilibrium potential of the solid solution. In this case, illustrated schematically in Figure 360b, both phases may dissolve at an accelerated pace, and this will lead to a thickening of the grain boundaries as a result of intercrystalline corrosion.

As the tempering temperature rises and the holding time increases, the precipitating carbide becomes richer in chromium, and its equilibrium potential shifts upward (to the right). If the potential has shifted, for example

at the point φ_2' in Figure 580a, solution of the carbide phase will proceed at the rate $i_3 = i_0$, i.e., more slowly. Solution of both phases may also begin later on, but it will proceed at a very low rate. When thermodynamic balance is established, the equilibrium potential of the carbide may become equal to or somewhat more positive than the φ_1 . There will then be practically no intercrystalline corrosion. At the given temperature this will ensue after a certain time which is equal to the immunization period t_1 in Figure 574. With elevation of the tempering temperature (see Fig. 581) [795] to 900° , the amount of precipitating carbides increases, and thereafter their reverse solution begins (Fig. 581a). A considerable time is required thereby for the precipitation of an equilibrium quantity of carbides even at 800° (581b). This is what determines the trend of kinetic curve 1 of the beginning of intercrystalline corrosion in Figure 574. Only after tempering at temperatures above 850° , when stable carbides are probably precipitated directly from the solution, does the increase in their quantity cease to exert an effect, and no tendency of the steel to intercrystalline corrosion is observed (Fig. 574).

The quantity of the carbides affects intercrystalline corrosion primarily in relation to the grain size. With coarsening of the grain there is an increase in the quantity of carbides per unit surface of the grain. But it is, apparently, not merely a question of their average relative amount. It was demonstrated in [305] that in a steel with a fine grain, the carbides form an intermittent pattern around the grains, this apparently impeding the penetration of intercrystalline corrosion in depth. In steel with a coarse grain, on the other hand, the carbides are arranged along the boundaries in a more compact chain.

The role, deriving from our hypothesis, of the chemical composition of the steel is illustrated by Figure 580c. Let us say that, with the same composition of the carbide phase, which has the equilibrium potential φ_2 , and with the same lines of the anode and cathode currents 2 and 3 as in Figure 580a,

the solid solution itself has a more negative equilibrium potential ϕ_1' , that the overvoltage of the reduction on it is characterized by the line 4', and that the total reduction rate on both phases is characterized by the line

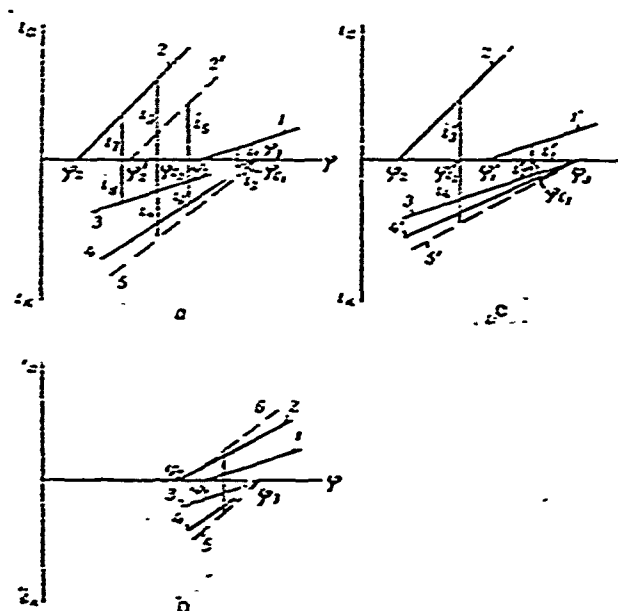


Figure 380. Diagrams of polarization curves illustrating the hypothesis of the nature of intercrystalline corrosion of austenitic steel.

5'. We see that in this case the carbide phase will be dissolved at the steady potential ϕ_{s2} and at the rate $i_3 = i_4$, i.e., lower than in the case of the solid solution in Figure 380a, which possesses in independent form a greater chemical stability (segments $i_1 = i_2$ are smaller than segments $i_1 = i_2'$). It is precisely the lower general corrosion resistance of the solid solution in steels containing 13% Cr as compared with high-chromium and chromium-nickel steels which, in our opinion, explains the circumstance that steels of the Kh13 type do not tend toward intercrystalline corrosion. The same fact may explain the lower sensitivity, noted earlier, of chromium-manganese-nickel steel to intercrystalline corrosion in comparison with chromium-nickel steels.

It does not, of course, follow from the foregoing that the tendency of steel toward general and intercrystalline corrosion under the influence of any factor must vary in different directions. As will be demonstrated somewhat further on, the catalytic electrochemical action of certain phases should, and in fact does, lead to simultaneous lowering of the resistance of steel to both general and intercrystalline corrosion.

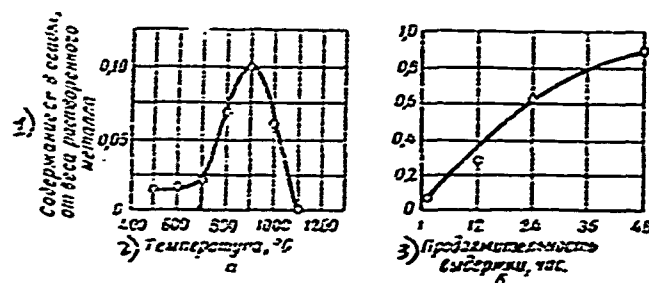


Figure 391. Effect of heating temperature and holding for one hour (a) and of the time of heating at 600° (b) on chromium content in the precipitate of steel containing 0.12% C, 19.9% Cr, and 8.56% Ni.

(1) Cr content of precipitate, percentage of weight of dissolved metal; (2) temperature, °C; (3) holding time, hours.

The positive effect of a diphasе gamma + alpha structure on the resistance of steel to intercrystalline corrosion is due, in our opinion, to the much higher rate of diffusion in the alpha phase as compared with the gamma phase. In consequence of this, in a steel with a gamma + alpha structure the carbides coagulate more rapidly and a smaller quantity of them is found on the grain boundaries. The positive effect of cold work, on the other hand, is apparently indirect. In contributing to the formation of the alpha phase and in facilitating the coagulation of the carbides in the same mechanical deformation intensifies the positive effect of the diphasе structure. Moreover, cold working increases the number of planes in the austenite along which the carbides may be precipitated, this being equivalent to refinement of the grain.

Finally, a word about the role of additional alloying of austenitic

steel with titanium (or niobium). It amounts, in our opinion, to the fact that the reduction reaction overvoltage on titanium carbides is inferior not only to that on metastable chromium carbides, but also smaller than on the solid solution, although it approaches the latter. Hence the titanium carbides, regardless of their own equilibrium potential in a given medium, will accelerate corrosion of the solid solution, i. e., lower the general corrosion resistance of the steel, as this in fact follows from Table 105. Titanium carbides will accelerate much more intensely the solution of metastable chromium carbides, through catalysis of the reduction process. Upon quenching from temperatures above 900° a part of the titanium carbides passes into solution and upon subsequent tempering is partly precipitated along the grain boundaries together with the chromium carbides (see the foregoing discussion). It is the accelerating effect of titanium carbides on the dissolution of chromium carbides and of the solid solution itself which causes intercrystalline corrosion.

It follows from the foregoing that the oxidation-reduction potential of the solution must also play a vital part. Hence one and the same steel may be found after the same heat treatment to be subject to intercrystalline corrosion in one solution and not subject to it, or less so, in another.

It is obvious from the standpoint discussed that intercrystalline corrosion may be caused by the presence on the grain boundaries of other phases, and not merely the carbides.

Thus, for example, sulfides precipitated along the grain boundaries may be the cause of intercrystalline corrosion of carbon steel. In acid-resistant steels, in consequence of their high chromium content, the most probable of such phases are the nitrides, which are precipitated in large quantity upon tempering even when nitrogen is present only in the form of a common impurity [see 785]. Certain observations justify the belief that the nitrides of chromium and titanium when coming in contact with the basic mass in stainless steel

possess a low corrosion resistance. Thus, it was observed [576, p. 128] in 18-8 steel that titanium nitrides were greatly corroded in 65-percent nitric acid and were completely dissolved 15 minutes after the beginning of the test. Experiments by Engineer S. B. Anisimov at one of the Leningrad mills have shown that nitriding of type 1Kh13 steel leads to a sharp drop in its corrosion resistance (nitriding is suggested for this steel also as a method of increasing its wear resistance). There are also other indications¹ of the extremely low resistance of nitrided steel in acid media.

Hence no surprise should be caused by the fact that a tendency toward intercrystalline corrosion has been observed in certain instances even in austenitic chromium-nickel steels in which the carbon content was less than 0.03% or even around 0.005%. Only the kinetics of the processes and the temperature dependence of their progress should be different in such cases.

Certain investigators [803] are also inclined to see the cause of intercrystalline corrosion of ferritic and semi-ferritic steels in chromium impoverished of the peripheral zones of the grains in consequence of precipitation of chromium carbides on their boundaries, taking into account, however, the simultaneous effect of the stresses arising upon rapid cooling of the steel from high temperatures. Others [for example, 802] assign the decisive role to the carbon-enriched austenite which is formed at the heating temperature and which decomposes on the grain boundaries upon subsequent rapid cooling of the steel. In this case the phase which is directly responsible for intercrystalline corrosion, in the opinion of some, comprises the chemically unstable iron carbides, which upon rectifying heating of quenched steel are transformed into chemically stable chromium carbides. In the opinion of others, it is the peripheral layer itself of the chromium-impoverished austen-

¹See the references in the paper by S. A. Balezin and V. B. Ratinov. DAN SSSR [Reports of the Academy of Sciences of the USSR], vol. 85, 1952, No. 2, p. 567.

the grain which is dissolved.

It should be noted, however, that the introduction into 17-percent chromium steels of a large quantity of elements which expand the region of the alpha phase, with the aim of preventing the formation of austenite at the heating temperature, has not eliminated the tendency of steels toward intercrystalline corrosion [793]. On the basis of these and the other results of their study, the authors of [793] consider the cause of intercrystalline corrosion of ferritic steels to be the stresses which arise in the surface layers of the grains as a result of precipitation of carbide or nitride phases. The heating of quenched steel at 650 to 800°, which relieves these stresses, restores the resistance of the steel to intercrystalline corrosion.

In analyzing the possible cause of intercrystalline corrosion of ferritic steels it is necessary, in our opinion, to take into account the fact that very brief heating is sufficient for their rectification. Although this may speak in favor of the stress theory, we feel that stresses cannot be the sole, or even the main, cause of intercrystalline corrosion in ferritic steels for the same reasons as in austenitic steels. For can the additional stresses caused by rapid cooling be responsible for intercrystalline corrosion. In fact, on the one hand, no intercrystalline corrosion is observed in ferritic steels upon very rapid cooling [793]. On the other hand, intensification of intercrystalline corrosion has been observed in partly ferritic steels [861] upon retarded cooling. At the same time, the immunization of steel upon rectifying heating, apparently, cannot be due to diffusion processes, which proceed at a low rate, for example, restoration of the chromium loss in the peripheral layer of the grains, change in the composition of the carbides, etc.

We believe that the processes causing intercrystalline corrosion are basically the same in ferritic and austenitic steels. In ferritic steels, upon rapid cooling from a fairly high temperature, a certain quantity of the phases which were partially dissolved upon heating, succeeds in precipitating

out onto the grain boundaries, where the thermodynamic and kinetic conditions are more favorable for this to occur than in the volume of the grains. Not only the carbides, but to an even greater extent the chromium nitrides, are such phases here. Thus, it has been established by experiment [785] that in a steel containing 27% Cr, 0.02% C of its total amount of 0.12% in the steel is retained in the solid solution after quenching from 1200°, while 0.05% of the total amount of nitrogen (0.055%) is fixed in the solution.

The significance of brief rectifying heating lies in our opinion in the fact that a large proportion of the carbides and nitrides is precipitated in the volume of the grain in this case. This reduces the catalytic activity of the basic mass, which comes in contact with the boundary phases, and this, in accordance with Figure 580c, should lead to weakening of intercrystalline corrosion. At the same time, the equilibrium potential of the basic mass will be shifted to the left (downward), which should lower the resistance of the grain and consequently intensify the general corrosion of the steel. It has recently also been demonstrated by experiment [681] that weakening of intercrystalline corrosion after brief rectifying heating is accompanied by intensification of corrosion of the grain itself, while longer holding, for example, for 30 minutes at 760°, imparts almost total stability to the steel. For ferritic steel, in which the rate of the diffusion processes is much higher than in austenitic steel, such heating is apparently sufficient to cause the composition of the precipitated phases to approach the equilibrium composition. The same processes occur if the steel is slowly cooled from a high temperature. The much more important role of the nitrides than that played in austenitic steel is, apparently, to be ascribed to the weaker effect of niobium in reducing the tendency toward intercrystalline corrosion in ferritic steels in comparison with austenitic steels. As regards titanium, its role in ferritic steels is basically the same as in austenitic steels. But since in ferritic steels the titanium must bind not only all the carbon, but also the increased

amount of nitrogen which the steels contain, more of it must be introduced than into austenitic steels, especially to eliminate intercrystalline corrosion in several media.

C. THE EFFECT OF ALLOYING AND OTHER FACTORS ON THE MECHANICAL PROPERTIES OF STAINLESS AND ACID-RESISTANT STEELS

Ferritic-martensitic steels

If high strength or hardness is required of stainless steel in addition to corrosion resistance, it must be receptive to martempering. Carbon-free ferrochromium alloys are already alpha alloys when they contain over 11 to 12% Cr (see Fig. 364). The maximum concentration of chromium rises considerably with increase in the carbon content of the alloy. Hence it is natural that the mechanical properties of high-chromium steel and the possibility of regulating them by heat treatment will be decisively determined by their carbon content. The combination of carbon and chromium is selected depending on the purpose of the steel, above all on whether the mechanical properties or corrosion resistance play the leading role for the articles manufactured from them.

Steels containing 25 to 30% Cr and possessing a very high corrosion resistance remain ferritic even when their carbon content is considerable (see Fig. 41). Hence the introduction into them of an increased quantity of carbon to augment the strength does not reach the goal, to say nothing of the fact that if melting is not conducted in vacuo (see [Russian] p. 545) they possess low plasticity, and especially low impact ductility, and are prone to 475-degree brittleness.

The hardness is increased to approximately 250 to 300 H₂ under the influence of carbon, due to the increase in the proportion of carbides in the ferritic basic mass. Upon the quenching of steel containing 25 to 30% Cr, even from high temperatures, as already pointed out, only about 0.02% C is fixed in the solid solution and almost all the nitrogen, which is contained

in the steel in the form of impurities. However, the precipitation of carbides and nitrides upon subsequent tempering did not in this case result in an increase, but rather a substantial decrease in hardness (from approximately 230 to 170 H₂ with a 0.12% C) [785]. It is possible, of course, that in these tests the maximum hardness value attributable to precipitation hardening remained unnoticed, since the tempering temperature was 800° at which the minimum holding time is one h r. But also in other studies, in which the hardness maximum in the tempering was observed (tempering at temperatures of 600 to 760°) and a minimum holding of several minutes) [681], the absolute value of the maximum was small and is not worthy of attention.

Hence steels containing 25 to 30% Cr are employed for articles of which a high resistance to violently oxidizing media or a high heat resistance is required. Such, for example, are the Soviet brands Kh25 and Kh18. The introduction of an increased amount of carbon into such steels is justified only when they are employed for shaped castings. In this case an increased amount of silicon is also found to be useful, since in an amount exceeding 0.6% the latter causes a discontinuous increase in the flowability [414, 496]. Steels containing 25 to 30% Cr still possess a fully satisfactory chemical stability even with an increased carbon content. At the same time, however, it is necessary to contend with their low impact ductility and poor weldability.

In ferritic-austenitic steel containing 26% Cr, 4% Ni, and 1.5% Mo and possessing an even higher corrosion resistance than ferritic steel (the American steel 329; see [Russian] p. 613), the hardness and strength may be appreciably increased by precipitation hardening due to precipitation of the sigma phase (Fig. 382). The hardness rises with increase in the chromium content, and, accordingly, the quantity of the sigma phase. After holding for 6 to 25 hours even at 760°, i. e., beyond the maximum, it is possible to obtain a hardness of 30 to 40 H_C and an ultimate strength of around 120 kg/mm². However, as is to be expected, rise in hardness and strength is accompanied

by lowering of the impact ductility, the absolute value of which decreases with increase in the chromium content [879]. The drop in impact ductility after heating to a temperature above 900° is ascribed by the authors to the formation of acicular austenite upon cooling. The corrosion resistance of the steel is also lowered after precipitation hardening, chiefly in consequence of precipitation of the sigma phase.

If the steel is intended for the manufacture of stainless tools, then its carbon content must be sufficient not only to ensure the possibility of martenspering, but also for achievement of the required high hardness of the martensite. Recently conducted studies [887] confirm the fact that even in high-chromium steels the maximum hardness after quenching depends basically on the carbon content, while chromium and other alloying elements scarcely affect it. An appreciable additional increase in the maximum hardness is caused by nitrogen, this being confirmed by other studies as well [898], apparently because it, just as carbon, is implanted in the lattice. The following empirical formula is proposed for approximate determination of the maximum hardness of quenched high-chromium steels, with account taken of their carbon and nitrogen content: $15 R_C = 2.182 + 0.469 (1g C) + 0.108 (1g C)^2 + 0.164 (1g N) + 0.025 (1g N)^2$.

Maximum hardness values of 50 to 55 R_C , which are achieved when the steel contains 0.3 to 0.4% C, are adequate for many instruments, such as those used in medicine. Such instruments are manufactured from the 3Kh13 and 4Kh13 steels, i.e., ones containing on the average 13% Cr and respectively 0.3 and 0.4% C. Instruments of which a higher maximum hardness is required, as well as stainless ball bearings, etc., should be manufactured from a steel containing 0.9 to 1.0% C. It is found necessary in this case to increase the chromium content to 17 to 19% in order to compensate for the negative effect of carbon on the corrosion resistance of the steel. The Kh18 steel, which contains 0.9 to 1.0% C and 17 to 19% Cr, may serve as an example. Use is made in the

USA for these purposes of several steels containing on the average 17% Cr and 0.7 to 1.1% C, up to 0.75% Mo being introduced into them with the aim of additionally increasing the corrosion resistance.

Since the martensite in such steels possesses a high stability toward tempering, after quenching they are subjected to tempering at 300 to 350°, and sometimes even at 400°. It is also recommended that high-carbon steels be subjected to cold treatment at -80° before tempering, for the purpose of more complete transformation of the retained austenite. One may consider 1000 to 1025° to be the optimum quenching temperature for medium-carbon steel and up to 1050° for high-carbon steel. It is to be seen from Figure 363 [784] for 3Kh13 steel that quenching from a temperature above 1000 to 1025° does not increase the hardness. There is also only a slight increase in the corrosion resistance in this case. At the same time, heating to higher temperatures involves the danger of coarsening of the grain, which leads to a sharp drop in plasticity and ductility of the instrument.

Either steel of the Kh17 type or that of the 1Kh13, 2Kh13, and 3Kh13 type are most commonly used as structural ferritic-martensitic stainless steels, depending on the strength and corrosion resistance values required.

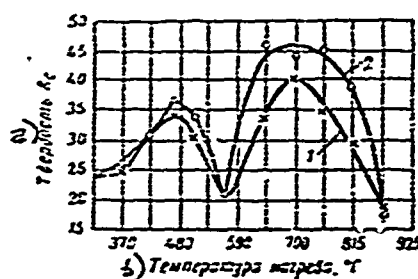


Figure 362. Change in hardness upon precipitation hardening of high-chromium steel containing nickel and molybdenum due to precipitation of the sigma phase: 1 - steel containing 0.21% C; 0.83% Mn, 0.4% Si, 27.41% Cr, 3.91% Ni, 1.55% Mo, 0.08% Nb; 2 - steel containing 0.11% C, 0.87% Mn, 0.46% Si, 29.69% Cr, 3.97% Ni, 1.44% Mo, 0.08% Nb [879]. (a) Hardness, HRC; (b) heating temperature, °C.

The Kh17 steel, which possesses sufficient corrosion resistance in a number of aggressive media plus average strength and high plasticity, contains up to 0.12% C and is partly ferritic. It is usually used after annealing at 750°.

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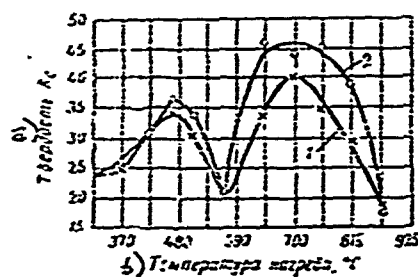


Figure 382. Change in hardness upon precipitation hardening of high-chromium steel containing nickel and molybdenum due to precipitation of the sigma phase: 1 - steel containing 0.21% C; 0.33% Mn, 0.4% Si, 27.41% Cr, 3.91% Ni, 1.35% Mo, 0.056% Nb; 2 - steel containing 0.11% C, 0.87% Mn, 0.46% Si, 29.69% Cr, 3.97% Ni, 1.44% Mo, 0.088% Nb [879].
(a) Hardness, H_{RC} ; (b) heating temperature, °C

The Kh17 steel, which possesses sufficient corrosion resistance in a number of aggressive media plus average strength and high plasticity, contains up to 0.12% C and is partly ferritic. It is usually used after annealing at 750°.

However, quenching of such steel from 1000 to 1100°, especially when it contains over 0.06% C, as may be seen from Table 106 based on the studies of A. A. Babakov [803], substantially improves the mechanical characteristics in consequence of the fact that the carbon-enriched austenite phase decomposes upon rapid cooling in forming dispersed structures. Appreciable increase is observed even in a steel containing 0.055% C. This may apparently be ascribed to the effect of nitrogen, which is usually not taken into account and an increased amount of which is usually contained in high-chromium steels. Quenching from higher temperatures again lowers the strength, since the quantity of the gamma phase at the heating temperature decreases, in conformity with the structural diagram. If titanium is introduced into the steel with the aim of reducing its tendency toward intercrystalline corrosion, the steel becomes

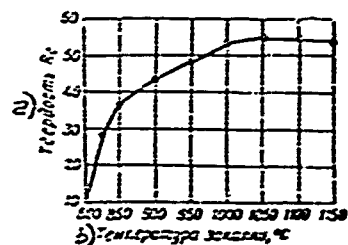


Figure 383. Hardness of 3Kh13 steel versus quenching temperature. (a) hardness, H_C ; (b) quenching temperature, °C.

ferritic, since titanium binds the carbon and nitrogen in stable carbides and nitrides. Hence the mechanical properties of the Kh17 steel scarcely differ after quenching and after annealing, if the quantity of titanium is at least greater than five times the carbon content [803]. Ferritic steel containing titanium has an elevated critical brittleness point, this leading to low impact ductility values at room temperature [803]. Changes in the impact ductility after tempering at 650° have also been observed in quenched low-carbon 0Kh17 (and 0Kh13) steel [806]; however, this calls for more accurate determination.

Steels of the 1Kh13, 2Kh13, and 3Kh13 type may possess a wide range of

strength characteristics plus satisfactory corrosion resistance which depends on the carbon content, after shorttempering and after high temperature anneal. It is to be seen from Figure 164 [90] for a steel containing about 13% Cr and 0.24% C, i.e., one lying on the boundary between the brands 2Kh13 and 5Kh13, that the yield point and ultimate strength begin to drop after tempering at a temperature above 500°. An appreciable increase in elongation and contraction also begin at approximately this temperature. The impact ductility undergoes a drop over the medium range of tempering temperatures, approximately up to 550°, and then it also rises.

Table 106.

Effect of Water Quenching on Strength Characteristics of Kh17 Steel With Similar Carbon Content

Heating temperature, °C	Length of holding period, min.	Strength (σ_b - numerators, σ_s - denominators, kg/mm ²) of Kh17 steel with carbon content, %, of			
		0.035	0.047	0.061	0.09
1200	5	33.9	67.1	73.3	92.0
		39.3	54.0	71.2	82.9
		51.9	69.2	82.3	93.6
1100	10	39.1	53.1	65.5	83.1
		56.9	69.4	81.6	86.8
		39.2	54.2	67.4	71.3
900	15	48.5	59.7	52.2	67.8
		31.6	42.9	35.4	52.7
		42.5	45.0	45.6	47.5
800	20	27.1	27.8	28.6	29.2
		42.7	45.2	47.7	45.0
		26.6	27.4	28.8	26.4

The drop in impact ductility is apparently the result of the same processes which cause irreversible brittleness upon the tempering of structural steels, but in this case they are displaced toward the higher tempering temperatures. This is attested indirectly by the different degree of drop in impact ductility not only in steels with different carbon content, but also in differ-

ent melts of the same composition. No drop whatever in impact ductility is observed in some melts at room temperature. But in all cases the drop increased with lowering of the test temperature (with the exception of very low temperatures, at which the impact ductility value is very small). This is illustrated by the isothermal curves in Figure 385 [90]. Noteworthy in this diagram is the fact that in specimens tempered over the brittle range the relative quantity of fibrous component in the fracture increases at higher test temperatures.

Thus, the drop in impact ductility is apparently related to elevation of the critical brittleness point. In fact, as may be seen from Figure 386 [90], which pertains to the same steel as does Figure 384, the critical brittleness point, determined both by the proportion of crystallinity in the fracture and by the impact ductility value, has a pronounced maximum at the tempering temperature of 550° .

Since the corrosion resistance of these steels also increases considerably after tempering at temperatures above 600° , they are usually subjected to tempering at 650 to 700° , depending on the properties required. As regards the quenching temperature, for steels containing up to 0.25% C 950 to 975° may be considered the optimum, and 975 to 1025° for steels with a higher carbon content. Further elevation of the quenching temperature, while not making substantial change in the chemical properties, leads to coarsening of the grain. This causes a lowering of the steel plasticity and elevation of the critical brittleness point after high tempering (Figs. 384-386).

Since carbon lowers the corrosion resistance of high-chromium steels, utilization of the higher strength of steel with an increased carbon content does not always prove possible. Steels of the 1Kh13, and especially the 1Kh17 type, possess a strength which is inadequate for many purposes. A combination of high strength and high corrosion resistance may be achieved by other

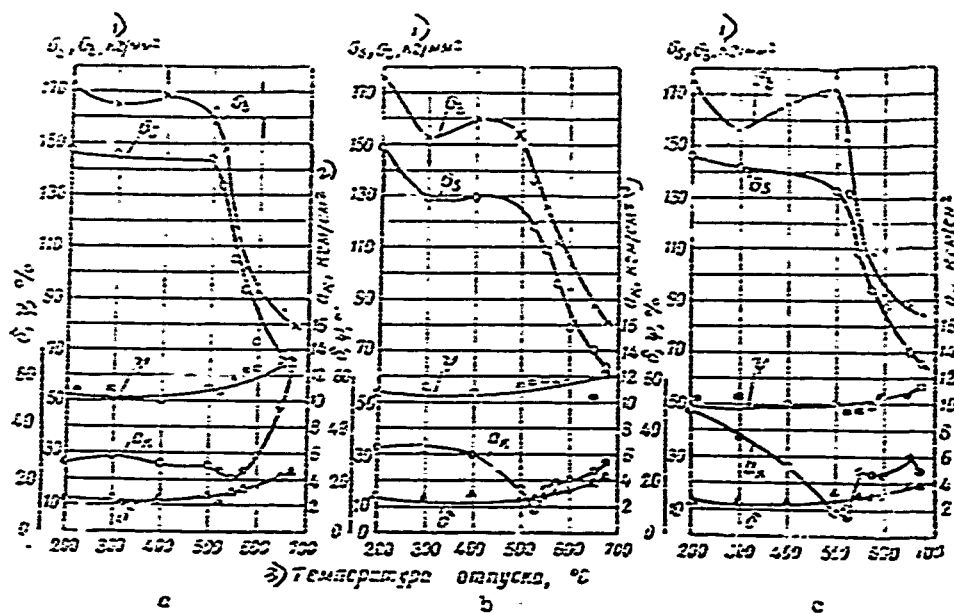


Figure 364. Mechanical properties of steel containing 0.24% C and 17% Cr versus tempering temperature after quenching from various temperatures. Quenching temperature:

a - 950°; b - 1050°; c - 1150°;

(1) σ_s , σ_b , kg/mm²; (2) δ , ψ , %; (3) tempering temperature, °C.

means, chiefly by decarburization and additional alloying.

The first method consists of subjecting finished articles of stainless steel with increased or high carbon content to surface decarburization. One such method may be decarburization by means of coating applied to the article (for example, of $MgCO_3$ or a mixture of 15 to 50% iron ore + 85 to 70% MgO) at 1050 to 1100°, the length of the holding time depending on the carbon content of the steel [495]. It has also been proposed¹ that decarburization be carried out by heating the articles in vacuo in the presence of special reagents. The mechanical properties of the core deteriorate only slightly as a result

¹Japanese patent 3509, June 9, 1954. Chem. Abstr., v. 49, 1955, No. 10, p. 5610.

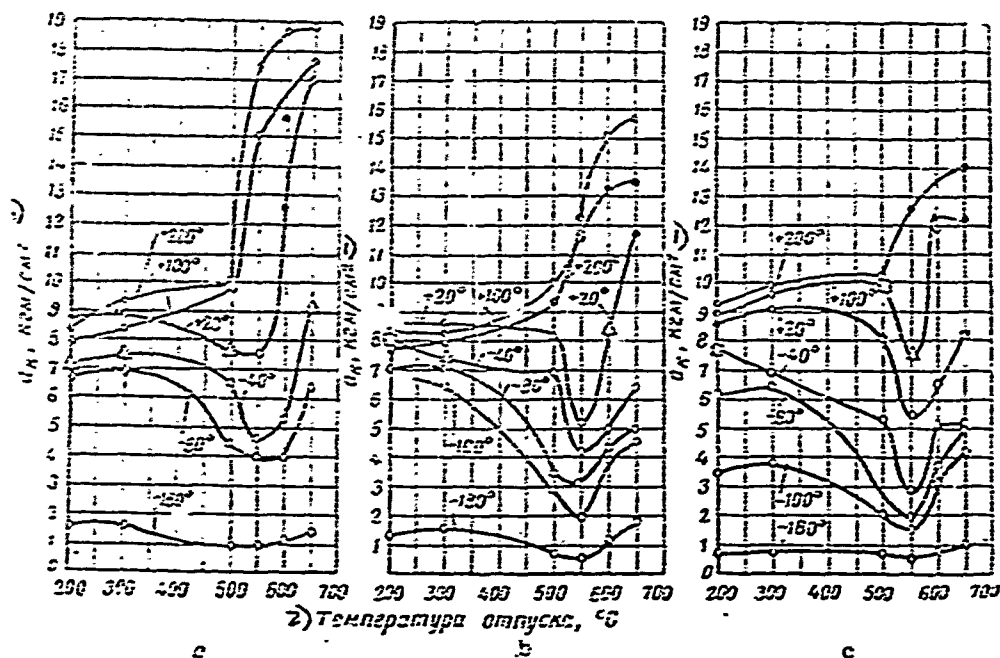


Figure 385. Impact ductility of steel containing 0.24% C and 13% Cr at various test temperatures versus tempering temperature. Quenching from temperatures of:

a - 950°; b - 1050°; c - 1150°. Arbitrary designation of relative content of fibrous component in fracture: \bullet - 100%; \square - 75%; \blacksquare - 50%; Δ - 25%; \circ - 0%.

(1) A_K , KJ/m²; (2) tempering temperature, °C.

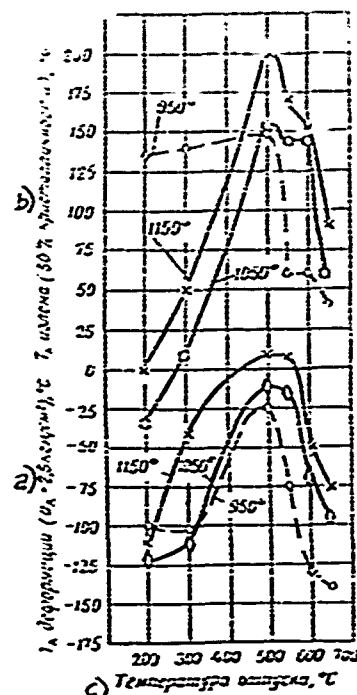
of holding at the decarburization temperature. On the other hand, the corrosion resistance in nitric acid, regardless of the carbon content of the core, is practically the same as that of a steel containing 0.09% C.

Another more convenient way consists of additional alloying of stainless steel with elements which, while scarcely impairing the corrosion resistance, intensify its receptivity to quenching through increase in the amount of the gamma phase at the heating temperature, or which increase the stability toward tempering. The most effective of these elements are nickel in an amount up to around 2.5%, copper, nitrogen, and niobium.

The introduction of nickel in an amount of around 2% transfers

Figure 366. Values of critical brittleness point T_c of steel containing 0.24% C and 13% Cr versus tempering temperature after quenching from various temperatures.

(a) T_{c_d} of deformation ($\sigma_k = 2.5 \text{ kg/cm}^2$), $^{\circ}\text{C}$; (b) T_c of fracture (50% crystallinity), $^{\circ}\text{C}$; (c) tempering temperature, $^{\circ}\text{C}$.



to the group of hardenable steels a steel containing approximately 20% Cr and 0.2 to 0.25% C, which does not respond to quenching if no nickel is present in it. In practice it is naturally more advantageous in adding nickel to produce a steel which, in addition to high strength, possesses increased chemical resistance, particularly to a large number of media. The brand Kh17H2 may serve as an example of such steel. Similar steels are employed in all countries.

A combination of even higher chemical stability, which in certain media approximates the stability of austenitic steel, with a capacity for considerable strengthening is achieved in steels containing 0.08% C, 0.4% Si, 0.6% Mn, 17% Cr, 4.2% Ni, and 2.75% Mo (the American non-standard steel AX-350) or 0.04% C, 17% Cr, 3.5% Ni, and 3.5% Cu (the American steel 17-4H). The structure of the first named of these steels is almost entirely austenitic after air cooling from a high temperature. It is thus recommended that for purposes of

strengthening it first be subjected to cooling down to a temperature of -65 to -75° , with the aim of transforming the greater portion of austenite into martensite, and then to temper it at $+50^{\circ}$ [378]. Martensitic decomposition of the greater portion of austenite may also be achieved by cooling from $700-725^{\circ}$. This treatment also is followed by tempering at $+50^{\circ}$.

The other steel (17-4PH), which is strengthened by precipitation hardening, due to the cuprous phase acquires the properties shown in Table 107 [809] after tempering. Tempering at a higher temperature lowers the strength of the steel, but the plasticity and corrosion resistance of the steel increase. The plasticity of this steel may be increased, and the hardness accordingly decreased, by the additional introduction into it of 0.25 to 0.45% N.

Table 107

Mechanical Properties of Structurally Hardening Stainless Steel Containing 0.04% C, 17% Cr, 5.5% Ni, and 3.5% Cu in the Form of Billets and Wire (Wire Rod)

Number of treatment	Treatment	$\sigma_{0.2}$ kg/mm ²	σ_b kg/mm ²	δ ($l=50$ mm) %	ψ %	Hardness H_C
1	Annealing at 1025 to 1050 ^o	77.5	105.5	8	45	34
2	Tempering 1 to 4 hours at 470 ^o	125.0	155.6	11	45	42
3	Tempering 1 to 4 hours at 540 ^o	112.5	119.5	14	54	37

It should be borne in mind, however, that strengthening of these steels is accompanied by lowering of their corrosion resistance [see 770].

As regards a steel containing 13% Cr, alloying it additionally with nickel increases the strength the most perceptibly in the case of slow cooling in the quenching process. The more rapid the cooling, and, in particular, the smaller the cross-section of the article, the lesser is the effect of strengthening after tempering caused by the nickel. At the present time, nickel is introduced into steel containing 12 to 13% Cr apparently only in

the USA and in England. The introduction of nickel into such steel in Germany was discontinued during the second World War.

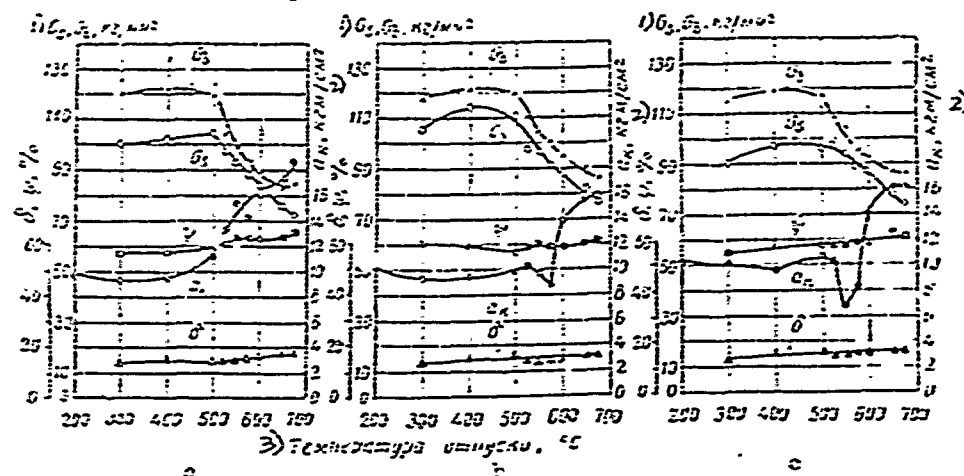


Figure 387. Mechanical properties of steel containing 0.1% C, 13% Cr, 2.6% Ni, and 0.1% Nb versus tempering temperature after quenching from various temperatures: (a) 950°C; (b) 1050°C; (c) 1150°C.

(1) σ_s , σ_b , kg/cm²; (2) a_5 , kg/cm²; (3) tempering temperature °C.

It is the most expedient to additionally alloy steel of the 1Kh13 type, which, in consequence of its low carbon content, possesses increased corrosion resistance and impact ductility and lower critical brittleness point, but a strength which is inadequate for many applications. Research by B. Ye. Sonin demonstrates that this can be achieved by introduction into 1Kh13 steel of niobium in the amount of about 0.1%, in view of the fact that the latter increases the stability of steel toward tempering. Simultaneous alloying of such steel with nickel widens the gamma region and increases the hardenability, and provides additional corrosion resistance. In comparing the properties of the steel containing 0.24% C and 13% Cr (Figs. 384 and 386) with the properties shown in Figures 387 and 388 [901] for a steel containing 0.1% C, 13% Cr, about 2.6% Ni, and 0.1% Nb, it may be seen that after high tempering, for example at 650°C, both steels have practically identical strength and plasticity values

(with the exception of a slight difference in elongation). At the same time, in the steel with 0.1% C and 0.1% Nb the impact ductility is higher and, what is even more important, the critical brittleness point is much lower, than in the steel containing 0.25% C and no niobium. The first steel is also less sensitive to overheating with elevation of the quenching temperature. The data of Figures 387 and 388 refer to specimens of small cross-section. Hence the effect of nickel is hardly manifested here and the admixture of 0.1% Nb plays the leading role.

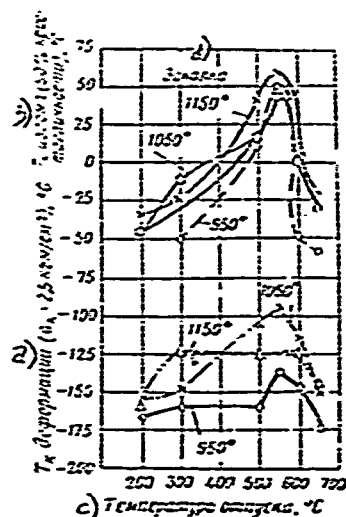


Figure 388. Values of critical brittleness point T_c of steel containing 0.1% C, 1.5% Cr, 2.6% Ni, and 0.1% Nb versus tempering temperature after quenching from various temperatures.

(a) T_c of deformation ($a_2 = 2.5$ kg/cm²), °C; (b) T_c of fracture (50% crystallinity), °C; (c) Tempering temperature, °C; (d) quenching.

Copper in the amount of 1 to 2% has no effect on the resistance of steel containing 1.5% Cr in nitric acid, while it increases the resistance in certain other acids. However, the absolute values of the weight losses of steel alloyed with copper are not small enough to render the steel resistant to these acids, and the effect of copper on the mechanical properties after high tempering, when it increases the corrosion resistance, is not great. Hence the utilization of copper as an additional alloying element with the aim of increasing the hardenability and strength of stainless steels has not become widespread, with the exception of cases in which it is introduced with the aim of imparting capability of precipitation hardening to the steel. In-

so far as we know it is only in the USA that steel containing 20% Cr and 1% Cu (designated 4-5) is used as non-standard [see 877].

Nitrogen, which greatly increases the limiting concentration of chromium, at which the gamma region is closed on the structural diagram, may be highly effective for purposes under review. The data in Table 108 show that in 15-percent steel after quenching and tempering, as well as in ferritic and semi-ferritic steels not subject to quenching, nitrogen substantially increases the yield point and ultimate strength without lowering the plasticity and impact ductility. In ferritic steels nitrogen even increases the plasticity and impact ductility considerably, this being attributable by its effect, already known to us, to refinement of the grain. Improvement of the impact ductility of the steels Kh17 and Kh28 by nitrogen was confirmed in a recent study [598], but it was found that the nitrogen content of Kh28 steel for this purpose must be greater than 0.4%; this calls for verification. The resistance of the steel to corrosion is not lowered under the influence of dissolved nitrogen.

Table 108

Effect of Nitrogen on the Mechanical Properties of High-Chromium Steels of Various Classes

Content of basic elements, %			σ_s , kg/cm^2	σ_b , kg/cm^2	δ , %	ψ , %	a_k , kg/cm^2	Hardness H_B	Source
C	Cr	N							
0.07 0.07	13.44 13.19	0.025 0.08	30.0 47.0	55.0 63.5	30 26	71 66	23.3 23.0	137 179	[490]
0.10 0.18	17.25 18.46	0.031 0.17	33.0 47.3	54.0 72.2	28 25	56 57	11.1 13.9	140 174	[490]
0.21 0.21	23.2 23.2	— 0.12	27.2 37.0	39.2 51.5	0.5 5.8	— —	0.45 8.0	176 205	[414]

The carbide-forming elements, in contrast to nickel and nitrogen, have a ferritizing effect on the structure of steel, both because they isolate the carbon in enriching the basic mass with chromium, and because a part of them, which is dissolved in the matrix itself contributes to contraction of the gamma region. The carbide-forming elements should thus have a dual effect on the strength of stainless steel. Ferritization reduces the hardenability, or deprives the steel entirely of its susceptibility to quenching. The presence of a large quantity of carbides, on the other hand, as well as of a certain amount of the alloying element in the solution, strengthens the ferritic matrix. Consequently, if stainless steels are compared in the annealed state, it is found that the carbide-forming elements should increase the strength the more intensely, the closer is the structure of the steel to ferritic. If the steels are compared after quenching and tempering, on the other hand, the results should be the opposite, as indeed is observed in reality [see 941]. In addition, there is a great drop in the impact ductility in this case.

But if the contents of such elements as, for example, molybdenum and titanium is high in a high-chromium steel, then they may impart to the latter the capability of being hardened by precipitation hardening, either through the agency of the sigma phase, whose formation they favor, or through metallic compounds. This effect is exerted, in particular, by molybdenum, which facilitates the formation of the sigma phase in steel with 26% Cr alloyed with nickel (see Fig. 582).

Austenitic steels

Acid-resistant austenitic steels, including steel of the 18-8 type, are characterized by high plasticity and ductility, low proportionality limit and yield point, the hypothetical cause of which was set forth on [Russian] p. 215. The ultimate strength of austenitic steels, on the other hand, has relatively high values. This is a result of their high mechanical harden-

ability (large strengthening ratio) upon loading beyond the yield point, as well as of a certain amount of austenitic decomposition in the fracture area of the specimen. Austenitic steels have a very low permeability and high resistivity, and this widens the possible areas of their application in comparison with high-chromium ferritic-martensitic steels.

Austenitic steels, just as ferritic steels, cannot be strengthened by conventional martempering. But the presence of a certain amount of alpha phase in the structure leads to an increase in the yield point and lowering of the plasticity of the steel even if the alpha phase has not been formed in accordance with the martensite mechanism. However, the strengthening methods which are accompanied by the appearance of the alpha phase in the structure, to say nothing of the fact that they are not sufficiently effective, cannot be utilized in cases in which the steel is employed as a non-magnetic or as a heat resistant steel.

The most commonly used method of strengthening austenitic steel is work hardening, if the nature of the article and the method of its manufacture permit the use of plastic deformation. The changes in the properties observed in this operation are the consequence of two processes: the responsiveness of austenite to cold hardening which is much greater than that of ferrite, and partial transformation of the former into martensite (for further details see [504]). The part played by the latter factor is naturally the greater, the less stable is the austenite. Hence an increase in the content of nickel in chromium-nickel steel and of manganese in chromium-manganese-nickel steel weakens the effect of their strengthening in plastic deformation. Especially high ultimate strength values are obtained in a steel containing only 7% Ni and having austenite of low stability. With this nickel content, the ultimate strength of work-hardened steel is substantially increased with lowering of the chromium content to 17%, with no appreciable damage to the plasticity.

As has been demonstrated in a number of studies, nickel also lowers the

extent of strengthening of steel in work hardening because it reduces the mechanical hardenability of the austenite. Thus, it is for this reason that it is desirable to have the contents of nickel as close to 7% as possible in steel subjected to intense strengthening, for example, steel intended for the manufacture of corrosion-resistant springs, cold-rolled aircraft parts, etc. Steel containing 0.08 to 0.2% C, 16 to 18% Cr, and 6 to 8% Ni (in the USA, steel 301 or 17-7) has become the most commonly used material for the manufacture of such articles.

Nitrogen, carbon, and manganese, while increasing the stability of austenite, at the same time increase its responsiveness to cold hardening. Increase in the stability of the austenite by nitrogen may be seen from Figure 389 [502] from the change in magnetic saturation. It is to be seen from the illustration that the nitrogen intensifies the mechanical hardenability of the austenite. In fact, the curves reflecting the growth of ultimate strength with degree of reduction run parallel for 18-8 steel with no nitrogen and with 0.13% nitrogen. Since the magnetic saturation of the latter steel scarcely changes at a reduction up to 60 to 70%, i. e., no martensite is formed, then if the nitrogen were not to increase the mechanical hardenability, there should be a smaller increase in the ultimate strength than in steel containing no nitrogen.

The mechanical hardenability of austenitic steel of the 18-8 type, as may be seen from Figure 390 [see 883], is increased even more greatly by dissolved carbon than by nitrogen. In steels with a higher carbon content, the plasticity is also higher than in low-carbon steel. This, apparently, should be attributed to the smaller quantity of the martensite formed. Thus, it is found more advantageous in practice to use steels which may be more intensely hardened by cold work in view of their increased carbon content, despite the fact that their austenite is more stable.

The relative effect of the carbon bound in carbides and dissolved in

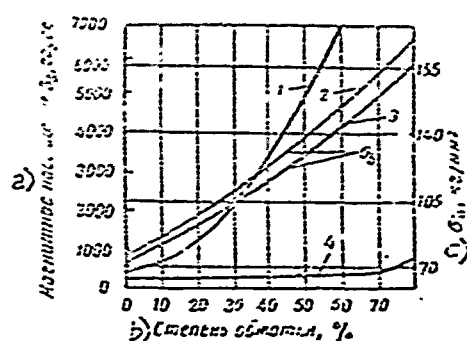


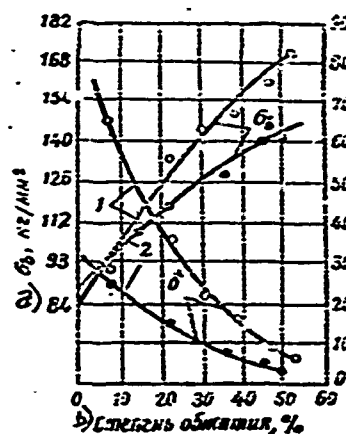
Figure 389. Effect of plastic deformation on ultimate strength and magnetic saturation of 18-8 steel with no nitrogen and with 0.16% nitrogen:

1 - B_S for 18-8 steel; 2 - σ_b for 18-8 steel + 0.16% N; 3 - B_S for 18-8 steel + 0.16% N.

(a) magnetic saturation B_S , gauss, (b) degree of reduction, % (c) σ_b , kg/mm^2

austenite on the strengthening of steel in work hardening is not yet sufficiently clear. It is known that elevation of the temperature of the preliminary hardening of 18-8 steel, which leads to complete solution of the carbides, reduces its hardness value upon cold working. Since the carbides cannot affect the mechanical hardenability of the austenite, this phenomenon could be explained by the fact that the stability of the austenite is lowered when free carbides, which impoverish the basic mass in chromium, are present. However, increase in magnetic inductivity, and consequent lowering of the stability of the austenite under the influence of work hardening with elevation of the preliminary quenching temperature, has been observed with Kh15N4G9 steel [835].

Figure 390. Effect of plastic deformation on strengthening of 15-7 steel containing 0.14% C (1) and 0.05% C (2); (a) σ_b , kg/mm^2 ; (b) degree of reduction, %



The austenite's own strengthening effect in cold-worked steel apparently is not only preserved, but even intensified in a number of cases in consequence of their combination upon plastic deformation. Thus, it is to be seen from comparison of Figure 391, a and b [886], that the difference in the yield point values which existed in the annealed state in steels 1Kh16N9T and 1Kh16N9 is maintained, while the difference in ultimate strength values is more than doubled.

The considerable increase in the mechanical hardenability of austenite caused by manganese is well known from the example of Hadfield's steel. Manganese also contributes to the strengthening of chromium-manganese-nickel steel by work hardening. Since carbon affects the mechanical hardenability of the austenite in the same direction, the yield point in the steel 1Kh15N4C9 (21100), which contains 0.15 to 0.30% C, is increased by work hardening to the same extent as in the steel 1Kh16N9 (Fig. 391a), although its austenite is stabler. At the same time, the 1Kh15N4C9 steel has a much higher ultimate strength, apparently because of the high value of the latter even in the initial state (Fig. 391c). This may also be explained by the high mechanical hardenability of this steel when loaded beyond the yield point. Apparently, because of the predominance of the role of work hardening over that of martensitic transformation, 21100 chromium-manganese-nickel steel strengthened by cold-working has a higher plasticity than chromium-nickel steels [498], even though the ultimate strength values are the same in both cases.

In chromium-manganese-nickel steel with a higher chromium content and lower carbon content than in the 21100 brand the mechanical hardenability of the austenite is increased by nitrogen. As may be seen from Figure 392 [675], the nitrogen-containing American steel 17-4-6 or the 201 (steel 1 in Table 102) is strengthened to the same extent as the chromium-nickel 17-7, while having a higher plasticity than the latter. On the other hand austenite in steel 201 is stabler than in the 17-7 brand as this is evidenced by the change

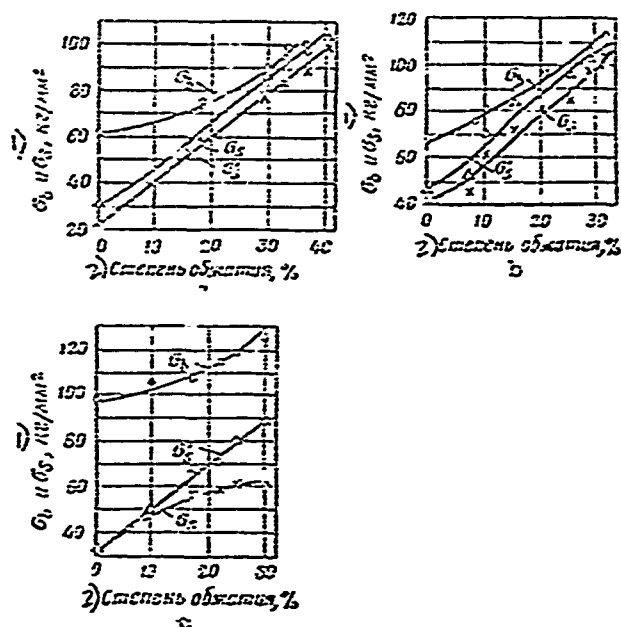


Figure 391. Effect of plastic deformation on the ultimate strength and yield point of austenitic steels:
 a - 1Kh18N9; b - 1Kh18N9T; c - 1Kh13N4G9;
 (1) σ_0 and σ_s , kg/mm^2 ; (2) degree of reduction, %.

in permeability of both steels upon work hardening, as illustrated in Figure 392b.

Due to the fact that the strengthening of austenitic steel upon deformation is also caused by partial transformation of the austenite into martensite, the temperature at which the deformation takes place has great effect on the extent of strengthening. Heating of steel, during its deformation, to 60-100-200° has the effect of reducing the strengthening, since in this case the latter is determined only by work hardening. Conversely, deformation at low temperatures greatly intensifies the effect of strengthening, since the latter is caused not only by cold working, but also by the formation of martensite [384]. Thus, an ultimate strength value of 60 kg/mm^2 was obtained in the case of drawing at 20°, and 140 kg/mm^2 in the case of drawing at -160°.

for a wire made of steel containing less than 0.15% C, 16 to 18% Cr, and 7% Ni (i. e., the 17-7 steel), the extent of reduction being 20% [305]. In general, however, the temperature at which plastic deformation yields the greatest strengthening effect depends on the position of the martensitic point.

Additional increase in strength is obtained upon the subsequent tempering of work-hardened steel. In particular, in the study cited [308], tempering at 400° of wire subjected to drawing at -160° with a 20% reduction increased the ultimate strength to 200 kg/mm². This effect is apparently the result of precipitation hardening by the carbides, facilitated by preliminary cold work, while the reverse alpha-to-gamma transformation had not yet terminated. Springs made of tempered wire can perform service for a lengthy period at temperatures up to 500°.

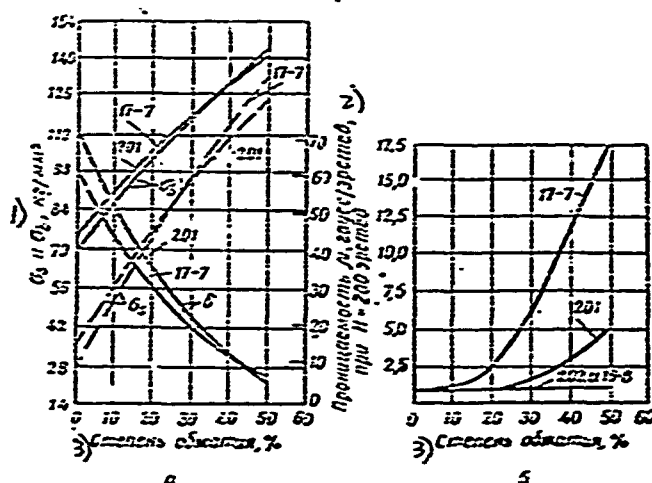


Figure 392. Effect of plastic deformation on the mechanical properties (a) and permeability (b) of chromium-manganese-nickel steel containing nitrogen (201, Table 102) in comparison with the chromium-nickel steel 17-7.

(1) σ_s and σ_b , kg/mm²; (2) permeability μ , gauss/cersteds, at $H = 200$ oersteds; (3) degree of reduction, %.

A highly important advantage of work hardening at low temperatures lies

in the fact that the required ultimate strength value is achieved at lower degrees of reduction than at room temperature. Owing to this fact, as may be seen from Figure 393 [357] for the steel 18-8, a higher plasticity may be achieved at the same ultimate strength value. By selecting a degree of reduction so as to assure that the values of the yield point and elongation be the same, such as 90 kg/mm² and 20% respectively (see Fig. 393), one can achieve higher ultimate strength value at low deformation temperature.

Recent studies show that a substantial increase in the strength of austenitic steel, especially its yield point, may be achieved by internal, phase hardening of the austenite in the process of direct and reverse martensitic transformation. It is to be seen from Figure 394 [769] that in a steel containing 0.05% C, 9.7% Cr, and 13.75% Ni, water quenched from 1100°, after the first cycle, which consisted of chilling of specimens from 750 to -193° (in liquid nitrogen), reheating to 750° for 30 minutes, and water cooling to 20°, the yield point was increased more than twofold, but the ultimate strength to a much lesser extent. Subsequent cycles produce but a slight effect. Hardening in this case, too, is accompanied by lowering of the impact ductility (Figure 394), but the value of the latter still remains very high. Such a method of hardening may be of practical interest for certain parts in cases where external cold working is impracticable because it involves changes in the dimensions and shape of the part.

In addition to work hardening, strengthening of austenitic steel may be achieved by additional alloying¹. The elements introduced in this case may affect the mechanical properties of the steel either directly, by entering the solid solution, or indirectly, by forming phases capable, in particular, of causing the effect of precipitation hardening.

¹It should be noted that bombardment with neutrons also increases the strength of steel of the 18-8 type and others.

Nitrogen may serve as an example of an element which strengthens steel of the 18-8 type by virtue of its solution in the austenitic matrix. It may be seen from Figure 595 [502] that the relative yield point $\sigma_{0.2}$ of 18-8 steel is increased by a factor of more than 1.5 when nitrogen is introduced in the amount of 0.04 to 0.11% (nitrogen scarcely affects the other mechanical properties of 18-8 steel), while further increase in the nitrogen content has

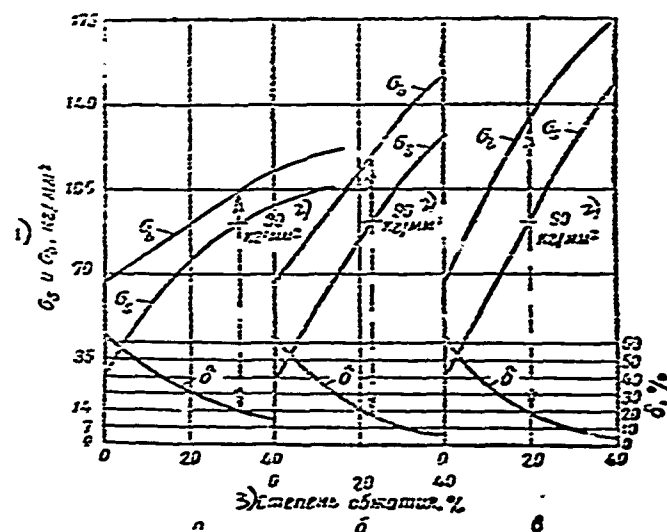


Figure 595. Effect of plastic deformation at low temperatures on the mechanical properties of 18-8 steel. Rolling at 20° (a), -78° (b), and -196° (c).

(1) σ_s and σ_b , kg/mm²; (2) 90 kg/mm²; (3) degree of reduction, %.

practically no effect. Hence a nitrogen content of 0.10 to 0.12% may be considered the optimum from the standpoint of strengthening. The effect of nitrogen in raising the yield point is also manifested in steel with a complete austenitic-ferritic structure, in which the initial values of this characteristic are correspondingly higher.

The same effect is exerted by nitrogen dissolved in austenite upon the yield point of chromium-manganese-nickel steel, as may be seen from the following example [502]:

C %	Cr %	Cr %	N %	Structure	σ_s , kg/mm ²
0.15	0.82	14.44	-	100% austenite	27.5
0.16	0.68	14.36	2 0.11	same	35.9

Carbon dissolved in austenite affects the strength of steel of the 18-8 type in the same direction as does nitrogen. However, carbon contributes much more indirectly to the strengthening of the steel, being present in the latter in the form of carbides. This follows from the example given in Figure 396 [497]. In the same steel after quenching from 600° the proportionality limit

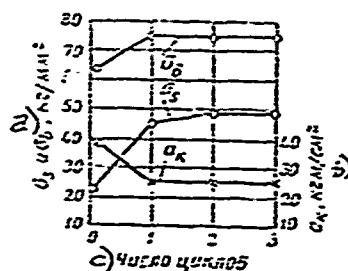


Figure 394. Effect of repeated cycles of direct and reverse martensitic transformation on the mechanical properties of austenitic steel containing 0.05% C, 9.7% Cr, and 13.73% Ni and quenched from 1100°.

(a) σ_s and σ_b , kg/mm²;
(b) δ , %; (c) number of cycles.

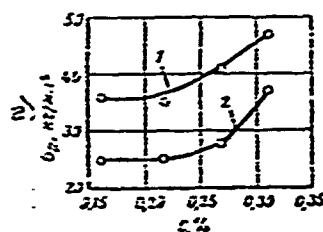


Figure 396. Effect of carbon on the proportionality limit of steel containing 17.4 to 18.1% Cr and 8.1 to 8.6% Ni: 1 - quenching from 900°; 2 - quenching from 900°.

(a) σ_s , kg/mm²

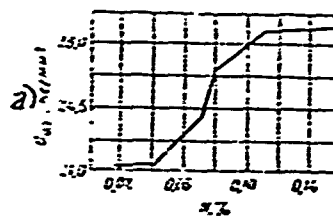


Figure 395. Effect of nitrogen in solid solution on the yield point of 18-8 steel.

(a) σ_s , kg/mm²

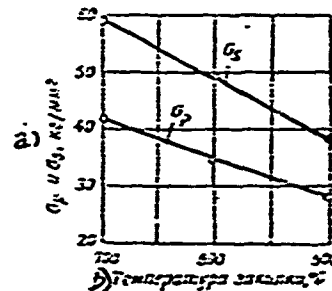


Figure 397. Effect of quenching temperature on proportionality limit and yield point of steel containing 0.46% C, 17.55% Cr, 8.13% Ni, and 3.85% Si.

(a) σ_s and σ_b , kg/mm²; (b) quenching temperature, °C.

is much higher in consequence of a greater amount of undissolved carbides than after quenching from 900° . The same is observed in chromium-manganese-nickel steel, as may be seen from Figure 397 [499].

The data of Figures 396 and 397 refer to the case of quenching of steel immediately after forging. If, on the other hand, the steel is quenched from a temperature higher than the line of solubility of the chromium carbides and then tempered, the variation curves of hardness and tensile strength become typical of the process of precipitation hardening. Preliminary work hardening, as always, accelerates the process. Thus, one can obtain very high strength values by combining cold work with precipitation hardening.

A disadvantage of aging steel of the 18-8 type by hardening through precipitation of chromium carbides is that the latter precipitate predominantly along the grain boundaries. This, in addition to intensifying intercrystalline corrosion, also leads to a sharp drop in plasticity and especially impact ductility. Precipitation of carbides within the grains, especially if it is oriented, also leads to lowering of the impact ductility, although it does not cause intercrystalline corrosion.

If a vigorous carbide-forming element is introduced into steel of the 18-8 type containing an increased amount of carbon, strengthening may occur owing to the carbides of this element. Table 109 [499] illustrates the effect of alloying steel of the 18-8 type with titanium on the mechanical properties of the former. In steel containing 0.16% C and 0.28% Ti, titanium binds about 0.06% C, and 0.1 to 0.12% C remains in chromium carbides. However, this steel has much higher proportionality limit (and yield point) values than a titanium-free steel containing 0.16% C, after quenching from 900° (see Fig. 396). This can be ascribed only to the additional strengthening of the steel caused by titanium carbides. It is for this reason that steels containing 0.8% and 0.9% Ti have very high proportionality limit and yield point values after quenching from 900° .

Table 104

Mechanical properties of steel containing on the average 18.4% Cr and 8.5% Ni, varying amounts of Carbon and Titanium, after quenching from 900° in Water.

C %	Ti %	$\sigma_{0.2}$ kg/mm ²	$\sigma_{0.2}$ kg/mm ²	$\sigma_{0.2}$ kg/mm ²	δ %	ψ %
0.18	0.28	32.0	40.5	82.0	33.0	60.5
0.23	0.53	39.0	46.5	97.0	49.0	57.9
0.32	0.91	44.0	42.5	98.0	38.0	58.6

The possibility has been established in a number of studies of increasing the tensile strength of steel of the 18-8 type by precipitation hardening due to the chemical compounds formed by such additional alloying elements as titanium (in the amount of 2 to 5%), beryllium, boron (in the amount of 0.5 to 1%), and aluminum. However, strengthening due to the first three, especially titanium and boron, is accompanied by a substantial lowering of the corrosion resistance. Corrosion resistance is reduced least of all by aluminum and a combination of titanium and aluminum in relatively small quantities.

The research of structurally-hardening corrosion-resistant steels based on chromium and nickel is actually focused on the utilization of these elements. A precipitation hardening steel (steel X or 322) containing on the average 0.07% C, 0.5% Mn, 0.5% Si, 17% Cr, 7% Ni, 0.7% Ti and 0.2% Al has been proposed in the USA [505]. In this steel the strengthening phase is soluble in austenite and difficultly soluble in the alpha phase, in consequence whereof the effect of precipitation hardening is the greater, the larger the quantity of the alpha phase in the structure of the steel. The average chemical composition of the steel is accordingly established in such a way as to assure a partial decomposition of austenite into the alpha phase upon air cooling from the quenching temperature. Titanium and aluminum bind a large proportion of the carbon and nitrogen contained in the steel, thus facilitating decomposition

of the austenite upon cooling from the quenching temperature, while an excess of these elements forms the strengthening phase.

Later, however, other steels were proposed there in which strengthening upon precipitation hardening is achieved owing to the phases formed by aluminum [809] or beryllium [892]. The following is the average composition of these steels: 0.07% C, 17.0% Cr, 7% Ni, and 1.1% Al (steel 17-7PH); less than 0.07% C, 19% Cr, 10% Ni, 3% Al, 3% Mo, 2% Cu, and 0.15% Be (steel V2B).

Moreover, the matrix composition of the second steel, especially the content of molybdenum, silicon, and copper, may vary within certain limits, depending on the purpose of the steel; for example: (1) 3.5% Si, 4% Mo, (2) 1.5% Si, 5% Mo, 3.5% Cu, (3) 3.5% Si, 3.5% Mo, 3% Cu. Comparison of the properties obtained after precipitation hardening in steels 17-7PH [809] and 322 [505], as shown in Table 110, reveals that the former possesses higher values of mechanical characteristics plus a higher plasticity than steel 322, and this renders it the one to be preferred.

After high-temperature treatment 1 (Table 110), the steels have an austenitic-ferritic structure and can be machined by cutting and respond to cold working with relative ease. During cooling from 700 to 750° (treatment 2), austenite decomposes at a temperature below 150° and the structure of the steels consists of martensite, ferrite, and residual austenite. The latter may be decomposed by chilling the steel to -60°. Tempering with the aim of achieving the precipitation hardening effect must ensue no later than an hour after treatment 2. After tempering at the highest of the temperatures indicated in Table 110, the mechanical characteristics obtained are lower, but the plasticity and corrosion resistance are higher. The steels may also be easily welded, being subjected to precipitation hardening after the welding. The steels retain their high tensile strength in service up to temperatures of around 400°.

Table 110

Mechanical Properties of Certain Precipitation Hardening Stainless Steels

Number of Treatment	Treatment	$\sigma_{0.2}$ kg/mm ²	σ_{b2} kg/mm ²	(δ_{50} mm) %	Hardness H _C
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Steel containing 17% Cr, 7% Ni, and 1.1% Al (steel 17-7 PH) in the form of sheets and strips¹

1	Annealing at 1065°	28.1	91.4	30	35
2	Treatment 1 + quenching from 750° (holding for 90 min).	70.3	102.0	9	31
3	Tempering for 1 hour at 460°	140.6	151.5	8	45
4	Tempering for 1 hour at 590°	130.1	140.6	9	43
5	Cold working	130.1	151.5	2	43
6	Cold working + tempering for 1 hour at 460°	166.7	175.8	1	49

Steel containing 17% Cr, 7% Ni, 0.7% Ti and 0.2% Al (steel 322) in the form of sheets and strips²

1	Annealing at 1000 to 1050°	52.5-80.5	84.0-105.0	4	22-28
2	Treatment 1 + quenching from 700°	49.0-77.0	84.0-105.0	6	23-29
3	Treatment 2 + tempering for 30 min. at 510°	94.5-122.5	108.5-129.5	6	35-41
4	Treatment 2 + tempering for 30 min. at 540°	87.5-115.5	101.5-122.5	6	34-40
5	Treatment 2 + tempering for 30 min. at 565°	77.0-87.5	94.5-119.0	6	31-37

- 1) In thin sheets and wire thinner than 1.75 mm, the σ_b is over 210 kg/mm².
 2) 0.75 to 1.5 mm thick. With a thickness of up to 0.75 mm, $\delta = 5\%$; greater than 1.5 mm, 7%. In rolled stock up to 12.5 mm in diameter, $\delta = 10\%$; over 12.5 mm, 12%.

3. ALLOYING OF STAINLESS AND ACID-RESISTANT STEELS WITH THE AIM OF IMPROVING THEIR TECHNOLOGICAL PROPERTIES

Stainless and acid-resistant steels, being high-alloy steels, possess lowered technological properties. Certain of the properties can be markedly

improved by additional alloying or modification of the steel.

For the purpose of improvement of the machinability of high-chromium and chromium-nickel steels, the same elements are added to them as are introduced for this purpose into conventional structural steel, i.e., sulfur, selenium, phosphorus, lead, bismuth; most frequently -- the first two. The Khl- "free-cutting" stainless steel containing 0.2 to 0.4% S, used in our country, may serve as an example. In certain countries -- England and the USA -- a combination of sulfur and selenium is added to the steel in order to improve the machinability by cutting. In the USA these elements are introduced not only into 15-percent chromium steel which is subjected to quenching and tempering, but also into 16-17 percent semi-ferritic chromium steel. In order to reduce the red brittleness, which is due to the increased sulfur and selenium content, frequently up to 0.6% molybdenum or zirconium is additionally introduced into the steel. The corrosion resistance of stainless steel, as has been demonstrated in particular by our research (in collaboration with B. Ye. Somin) is scarcely impaired at all under the influence of an admixture of sulfur or selenium. The overvoltage of the reduction reaction on the sulfides and on the solid solution in stainless steel, apparently, is roughly the same.

Improvement of the deformability in the hot state presents a serious problem for many acid-resistant (and heat-resistant) austenitic steels. Associated with this is not only a higher output of useful metal, but also the possibility of using larger ingots, the application of extrusion in place of pressing for the manufacture of pipes, and the like. For certain steels such as those alloyed with a large amount of molybdenum and copper, their very use as deformable steels, and not merely as cast ones, depends thereon.

The deformability in the hot state, especially during the first reductions, depends, as we know, not only on the composition of the steel, but also to a large extent on the quality of the ingot; on primary crystallization and

the mode of melting (chiefly on the method and conditions of deoxidation); the quantity, shape, and location of the non-metallic phases; and, consequently, on the impurities contained in the steel [see 888 et al.]. In particular, melting in vacuo greatly improves the deformability, basically because of the sharp drop in the quantity of non-metallic phases and their size [see 858]. Alloying elements can indirectly affect these factors as well, for example, by changing the position of the solidus line and the interval between the liquidus and solidus in which formation of the primary structure takes place in the process of solidification. The elements forming highly stable carbides and metallic compounds, which are frequently contained in large quantity in stainless (especially heat-resistant) austenitic steels, may impair the deformability because of these brittle phases, especially if they are located predominantly along the grain boundaries. The heat-resistance itself of austenitic steels also renders their hot deformation difficult and necessitates heating to higher temperatures.

Alloying to a large extent determines another highly important factor which affects the capability of austenitic steel to deform: this is the quantity of the alpha phase contained in this steel at the deformation temperature. It has been found in practice that with a content of the alpha phase in an amount corresponding to a grade higher than 5¹, i.e., greater than about 25%, the steel possesses a low plasticity and does not lend itself readily to forging, rolling, extrusion, cold drawing, stamping, etc. According to the observations of N. S. Alferova [869], the cracks forming upon hot deformation

¹We have adopted the evaluation of the quantity of the alpha phase based on the scale of the "Zaporozhstal'" plant (see V. Speranskiy, *Stal' [Steel]*, No. 4-5, 1959). A quantity of the alpha phase of up to 5% corresponds to grade 1; 5 to 12% to grade 2; 12 to 20% to grade 3; 20 to 35% to grade 4; and over 35% to grade 5. Zero quantity of the alpha phase is evaluated as grade 0.5.

in the 1000 to 1250° temperature range are located both along the grain boundary, but by preference along the inclusions of the alpha phase or the carbides.

The quantity of the alpha phase depends on the composition of the steel, the temperature, and the time of heating. It is to be seen from the cross section shown in Figure 366 of the Fe-Ni-Cr-C structural diagram for 18% Cr and 8% Ni, that when equilibrium is attained, i.e., in case of fairly long holding or very slow heating, the low-temperature (secondary) alpha phase must change into the gamma phase at temperatures above the GSK line. When the line I₁I is reached the high-temperature (primary) delta (alpha)-phase should appear. The quantity of the latter will increase with further rise of temperature to the solidus line and with lengthening of the holding time.

In changing the position of the corresponding lines on the structural diagram, the ferritizing elements contained in steel contribute to the growth of the alpha phase, and cause the temperature region of its stability to widen. Such elements include chromium itself when contained in an amount exceeding 16 to 17% (see Fig. 355), as well as titanium, molybdenum, silicon, aluminum, niobium, and others. Quantitatively the elements enumerated have a varying effect, but the majority of them produce a greater influence than chromium. titanium, molybdenum, silicon, and niobium have the greatest effect.

If the elements of this group simultaneously form stable carbides, then they promote the growth of alpha (delta)-phase not only in consequence of their solution in the matrix, but also because in binding the carbon in insoluble carbides they extract a portion of it from the solid solution. Consequently, if at the heating temperature the carbides are transferred to the solution, the presence of carbon in the latter will weaken the ferritizing effect of the dissolved element itself. This apparently may explain the very small quantity of the alpha phase formed at 1150° in 18-8 steel with a Ti-C

ratio of approximately 6 (Table 111 [5847]), since the greater part of titanium carbides passes into the solid solution at 1150°, as may be seen from Figure 376. With a Ti:C ratio greater than 6, the alpha phase displays an intermittent growth (Table 111) and subsequently its quantity rises sharply. Hence, when steel is alloyed with titanium for the purpose of increasing its resistance to intercrystalline corrosion, it should not be introduced in an amount greater than that required for binding carbon and nitrogen.

Table 111.

Content of Alpha (Delta)-Phase in Steel Containing Approximately 0.1% C, 18% Cr, 8% Ni and Titanium After Holding for 2 Hours at 1150° and Quenching in Water

Ti content, %	0.59	0.64	0.73	0.75	0.75
Ti/C	5.9	6.4	7.3	7.5	7.5
α(δ)-Fe, %	0.5	8.0	11.0	13.5	19.0

This principle also applies to niobium, i.e., the latter should not be introduced into steel in an amount greater than that needed to eliminate intercrystalline corrosion. There are contradictory data in the literature relative to the effect of niobium on the quantity of the alpha phase at high temperatures. According to some studies [889], the quantity of the alpha phase is approximately the same in steel of the 18-8 type containing niobium and titanium at temperatures of 1200 to 1350°. In other studies [584], on the other hand, it has been found that in 18-8 steel even when the Nb:C ratio is greater than 15 only about 3.5% of the alpha phase is formed after 4 hours of heating at 1350°, while at 1200° it is practically absent. These divergences are apparently due to a varying content of other elements, such as nitrogen, in the investigated steels and to failure to take other factors into account. But with approximately the same quantity of the alpha phase, niobium causes a much greater drop in the plasticity of steel at 1150 to 1250° than does titan-

and [807, 808]. This is illustrated in Figure 398 [807] by the change in the torsion angle with rising temperature in chromium-nickel steel alloyed with niobium (AISI 311B) and titanium (AISI 312), prior to the failure of specimens. This, apparently, is attributable not only to the negative effect of the dissolved niobium on the plasticity of austenite, but also to the fact that in steel of the 18-8 type niobium carbides are dissolved with difficulty even at 1300° as revealed in experiment [890].

Such elements as nickel, manganese, carbon, nitrogen, and copper exert their effect on the quantity of the alpha phase in the direction opposite that of the ferritizing elements. Manganese has a weaker, and carbon and nitrogen a stronger, effect than nickel, the effect of the carbon being somewhat greater than that of nitrogen. It should be noted that in a steel containing over 1% Cr manganese contributes to a reduction of the quantity of the delta (alpha)-phase only when it is contained in an amount up to approximately 6%. Further increase of its quantity in such steel, contrary to expectations, widens somewhat the region of the delta (alpha)-phase on the structural diagram [791, 895].

It follows from the foregoing that in steels, which by their average chemical composition approach the austenite stability boundary on the phase diagram (Fig. 353), the quantity of the alpha phase may vary greatly in different melts in consequence of the fluctuating chemical composition even within the limits of the same brand of steel, as this may be seen, for example, from Figure 399 [890] for a steel containing niobium. The conditions of cooling of the ingot, and consequently its dimensions as well, also affect the quantity of the alpha phase. The latter also is not uniformly distributed over the cross-section of the ingot [see 811, 812]. The smallest quantity of it is to be registered at the edges, with the bulk being located in the central part of the ingot [812]. This is also explained by dissimilar crystallization and cooling conditions prevailing in the different zones. Figure 400

[511] may serve as an illustration. It shows the kinetics of the alpha-phase growth at temperatures of 1250 to 1300° in the outer and central zones of initially cast-steel ingots from different heats. It also follows from Figure 400 that under certain conditions, particularly in case of short-term heating and small initial content of the alpha phase, the quantity of the latter may still be permissible even at 1300°, although ingots of 1Kh18N9T steel are normally not heated above 1250°-1270°. Keeping close to the lower temperature is recommended [512].

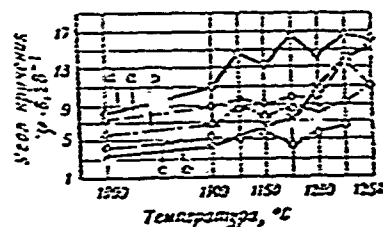
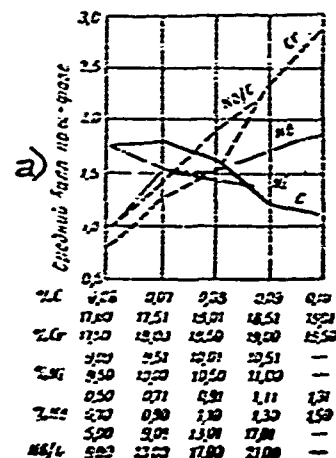


Figure 398. Torsion angle (prior to failure) at high temperatures in austenitic steels:
 a - NI402 (containing niobium), grade 1.0 according to the alpha-phase scale;
 b - same, grade 1.5; c - same, grade 3.0; d - 1Kh18N9T steel, grade 0 according to the alpha phase scale;
 e - same, grade 3.0.

Reduction of the alpha phase quantity by means of alloying can be achieved by several methods. One method consists of increasing the manganese content, its quantity in chromium-nickel austenitic steels usually being about 2% for this purpose. An increased nitrogen content produces a substantial effect. In steels with the indicated proportion of manganese and nitrogen, the quantity of the alpha phase is most frequently regulated by adjusting the contents of nickel. Thus, when the steel is additionally alloyed with ferritizing elements -- molybdenum, niobium, titanium, silicon, etc., -- the amount of nickel is increased accordingly. In melting steel of the same brand, it is more advantageous, for the purpose of saving nickel, to reduce the quantity of the alpha phase by lowering the content of chromium to the lower limit for the brand in question. Views were expressed in the Soviet and foreign literature to the effect that it is sufficient to assure a definite Cr:Ni ratio in steel in order to obtain stable austenite. However, this criterion cannot be considered well-grounded, because of the complex interatomic inter-

Figure 399. Alpha-phase grade in niobium-containing 18-8 steel versus chemical composition.

(a) average grade as per alpha-phase scale.



action of nickel and chromium in steel, as was discussed on p. 38. In particular, it follows from the diagram in Figure 355 that when the contents of chromium surpasses the 16-17% level, the Cr:Ni ratio necessary to prevent the formation of alpha-phase begins to decline (from approximately 2.2 at 16% Cr to approximately 1.25 at 50% Cr), i.e., the required relative quantity of nickel becomes even greater. Production and experimental data confirm the fact [see 313] that for the same Cr:Ni ratio, the quantity of alpha phase increases with rising chromium content.

Basically the same methods are employed to achieve stabilization of austenite and reduction of the alpha-phase quantity at the temperature of hot deformation in chromium-manganese-nickel acid-resistant steel. In steel Kh13Kh4G9, which is most widely used in the Soviet Union, this is ensured by a low chromium and higher (0.15 to 0.30%) carbon contents. A steel containing 0.06 to 0.10% C, 16 to 17.5% Cr, 3.5 to 4.5% Ni, 7 to 9% Mn, and 0.12 to 0.18% N has recently been proposed in the USA as a steel which is stable toward delta (alpha)-phase formation. According to the data of the authors [791], such a composition ensures a fully austenitic structure at a heating temperature no higher than 1225° even in cast steel, in which a greater amount of nickel and nitrogen is required for austenite stabilization than in rolled steel. With respect to corrosion resistance, such steel is approximately

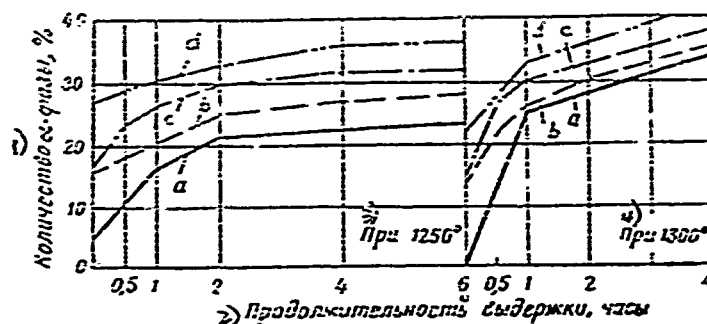


Figure 400. Quantity of alpha phase in cast LKh16K9Z steel versus holding time at 1250 and 1300°:

a - heat 1, edge of ingot; b - same, core of ingot;
c - heat 2, edge of ingot; d - same core of ingot;

(1) quantity of alpha phase, %; (2) holding time, hours; (3) at 1250°; (4) at 1300°.

equivalent to the chromium-nickel steel 17-7.

It is interesting to note that, in the opinion of the majority of Soviet and foreign researchers [see 790, 814], an increased amount of the alpha phase has a positive effect on another very important technological property: reduction of the tendency toward formation of hot cracks during welding. Yet, the role of this factor is denied in a number of studies [see 815]. Hence, elements contributing to alpha phase formation are introduced into welded joints of austenitic steels. The more so, since the resistance of a joint to intercrystalline corrosion is increased in the event of a diphasic gamma + alpha structure, as was pointed out earlier.

A highly effective method of improving the deformability of corrosion-resistant steels in the hot state consists in introducing additions of rare-earth elements, especially of cerium and lanthanum, or their oxides [see 792, 793, 899, etc]. Powerful deoxidizers such as a calcium-barium alloy, calcium-silicon, etc., are introduced at the same time in the latter case. The nature of the positive effect of the rare-earth elements has not yet been fully

established. At any rate, their effect is a many-sided one and consists in degasification, desulfurization (the latter determined by the free energy of formation of their sulfides; see Table 6), in sharp improvement of the primary crystallization of the ingot, and, apparently, in the alloying of the inter-crystalline layer.

What was said about such admixtures in application to heat-resistant steels is just as true of them and their effectiveness in corrosion-resistant steels. It can only be added that, according to published reports, it has been possible, by introducing rare-earth elements, greatly to improve the deformability of type 18-8 steel with 2.5% Nb, the structure of which contains about 30% δ or the alpha phase at the deformation temperature. It has also become possible to transfer to the category of deformable steels the steel 20, which is stable in sulfuric acid and contains 20% Cr, 25% Ni, 2% Mo, and 3% Cu (steel 3 in Table 103). This brand was formerly used in the USA only as a cast steel, since attempts to subject it to forging or rolling were unsuccessful [see 562].

Substantial improvement in the malleability of acid-resistant steel alloyed with molybdenum and copper, due to the destruction of the zone of acicular crystals in the ingot, and carbide and oxide-sulfide liquation, has been observed [616] upon the introduction of 0.2 to 0.8 Ca. A positive effect in this respect is also exerted by other elements, which perform the function of modifying agents. Finally, melting in vacuo produces a great effect, as was pointed out earlier. A combination of several methods may prove advantageous in a number of cases.